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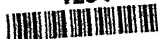
PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

JAMES H. GARDINER, F.C.S.

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THE CHEMICAL NEWS.

VOLUME CXXI.

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No. 3142.—JULY 2, 1920.

EFFECT OF PRESSURE ON GAS ADSORPTION.

By ALWYN PICKLES.

WORK was only done at pressures below atmospheric. Six kinds of charcoal in various states of division were studied in a manner similar to that of Macbain (*Phil. Mag.*, 1909, xviii., 816). The charcoals, previously heated to expel air, and in equal volumes (50 cc.), were saturated with dry ammonia at atmospheric pressure and room temperature. They were then placed, in turn, in a dry glass vessel closed with a rubber stopper carrying a manometer and aspirator tube. The apparatus had been previously tested and proved gas-tight. Capacity of vessel, 400 cc.

A good water-pump was used as aspirator, and as the necessary pressure was reached the aspirator tube was closed, using a screw clip. The pressure was noted at intervals, temperature being kept constant by having the vessel immersed in jar of cold water surrounded by non-conducting material. Experiments were done with each charcoal at two or three different pressures. Occasional blank experiments were done as a control.

The pressure in all cases at first increased and ultimately decreased, but this behaviour varied with the charcoal used.

The first effect of aspiration would be to remove the gas on the charcoal surface. The increase in pressure would therefore be due to escape of gas from the interior, subsequent decrease being due to renewed surface condensation.

In no case was the initial pressure regained, but the results give a good index as to the inner structure of the charcoals used. Thus, where rapid pressure increase is noted, a complex internal structure may be surmised—cocoanut, fruit stone, &c. In the case of birch dust its gas-adsorbing capacity depends mainly on surface effect. The palm nut charcoal used was in large pieces, so that most gas it retained would be by absorption.

Other Details.

1. Apparent density determined by weighing several definite volumes of charcoal and obtaining average mass per cc. Real density determined by specific gravity. Bottle method. In the following results apparent density is given first:—

Almond	..	0.48	1.70
Birch chips	..	0.23	1.44
Fruit stone	..	0.68	1.72
Birch dust	..	0.21	1.47
Cocoanut	..	0.63	1.71
Palm nut	..	0.64	1.59

1. Birch Chips.—

Time (mins.).	Pressures in centimetres, Hg.		
0	20.0	41.9	60.0
8	22.2	44.1	62.1
15	23.8	45.6	63.1
25	23.8	45.6	63.0
40	23.8	45.5	62.8
55	23.7	45.5	62.5

2. Cocoanut.—

0	20.4	40	59.7
8	22.8	42	60.2
17	24.3	43.2	61.8
40	24.8	43.6	60.5
60	25.1	43.3	60.3
80	25.0	42.8	60.2
110	24.4	42.7	60.2

3. Fruit Stone Dust.—

0	20	40.1	59.9
7	24	43.7	62.0
15	28	46.5	64.3
24	31.1	49.6	64.0
45	32.8	49.7	63.1
60	30.9	49.2	62.3
90	29.7	47.6	61.4

4. Palm Nut.—

0	20.5	60.1
8	23.1	62.0
20	24.3	62.6
45	24.3	62.6
60	24.3	62.5
80	24.3	62.5

5. Almond.—

0	20.0	48.7
8	25.8	52.7
15	28.6	54.5
25	32.1	56.9
50	34.2	56.4
75	33.4	55.0

6. Birch Dust.—

0	20.0	40.2
7	21.1	41.1
15	21.4	41.4
25	22.0	42.0
50	21.8	41.8
70	21.7	41.7

2. Carbon content determined by combustion and estimation as CO_2 . The content was generally about 85 per cent.

3. Moisture content of a charcoal was increased by addition of lime, common salt, or potassium carbonate. Unsatisfactory results were obtained as the mass tended to become sticky and unworkable. With phosgene, COCl_2 , the moisture would be advantageous, as decomposition into CO_2 and HCl would be assisted. Further, the water would serve as a reservoir for the HCl . This gas was not studied as it could not be got in sufficient quantities; also, laboratory class work could not be interfered with.

4. Porosity of a mass of charcoal dust was increased by mixing with solid ammonium bichromate and heating out of air. The efficiency against gases was increased per cc. of actual charcoal, but per cc. of whole product efficiency was low.

5. Decolorising power was tested, using caramel and indigo solutions, also highly discoloured crude glycerin. Birch charcoal dust was found a remarkably good decoloriser, but subsequent filtration was slow. Coarse charcoals do best at high temperatures, when penetration effect is considerable. Heating immediately before use drives from the charcoal any contained air or hydrocarbons, thus increasing the efficiency.

6. As gas adsorbents the denser charcoals were most efficient. The order of efficiency was found to be—palm nut, cocoanut, fruitstone. The values obtained by Hunter were not even approximately obtained. It is very probable that he used a highly specialised form of charcoal. State of division is an important factor. Fine dusts offer a large resistance to a gas and in large quantities there would be some difficulty in their use. Granules of about 1 mm. diameter were found suitable.

7. *Selective adsorption.*—Iodine residues were treated with chlorine water and iodine liberated removed by warming the solution with charcoal dust. The charcoal then filtered off and heated in an iron retort. The iodine sublimed into the neck of the retort and removed. The charcoal remaining was of little further use. In one case the charcoal was extracted with hot alcohol, but the process was slow and required a large volume of alcohol. The alcohol was subsequently distilled off from a water-bath, the iodine remaining. Both methods were found to be somewhat tedious in practice but fairly efficient as regards iodine yield. Iodine in iodates could be liberated by using bisulphite solutions after chlorine had liberated iodine from iodides and such iodine had been removed as above. Later, selective adsorption will be studied as a means of removing alkaloids from alkaline extracts of vegetable tissues.

8. Adsorption of iodine from its solution in benzene and of benzoic acid from benzene was studied. The iodine was removed to a small extent comparatively, 17 per cent. Since iodine in KI solution exists as the ion I_3 , and is removed to the extent of 80 per cent under the same conditions of temperature, &c., it is probable that iodine in benzene exists in a simpler form. Benzoic acid was removed to the extent of 80 per cent; this points to benzoic acid molecules being associated in benzene.

It was noticed throughout the preceding work that the more complex in structure a substance may be the more readily it is adsorbed by charcoal. This fact should be useful in the case of alkaloid extraction.

PHYSICAL APPARATUS FOR CANADIAN UNIVERSITY.—

A report has been received in the Department of Overseas Trade from His Majesty's Trade Commissioner at Toronto (Mr. F. W. Field) to the effect that a professor of a Canadian university desires to receive catalogues from United Kingdom manufacturers of physical apparatus for university laboratories for his guidance in placing orders. The name and address of the professor referred to will be furnished by the Department to any United Kingdom manufacturers interested, on application.

STRUCTURE OF MATTER AND THE QUANTUM THEORY.

SUPPLEMENTARY NOTE TO PART IV.

By F. H. LORING.

UPON further study I find that the scheme (CHEMICAL NEWS, cxx., p. 183) can be made quite regular up to and including nickel. The following table gives the additional values:—

S	32.06	32.07
Cl	35.50	35.46
A	39.88	39.9
K	39.07	39.10
Ca	40.06	40.09
Sc	43.50?	44.1
Ti	48.22	48.1
V	50.93	51.06
Cr	52.06	52.0
Mn	54.93	54.93
Fe	55.78	55.84
Co	58.93	58.97
Ni	58.77	58.68

The 1920 atomic-weights are given alongside the ones deducible by means of the scheme. The significance of Note 1 of Part IV. is now made more apparent.

The order of the elements in the above table is necessitated by the scheme, and this agrees with that given by the atomic numbers.

Argon resembles beryllium in its composition, having apparently *three* outliers.

Cobalt and nickel have isotopes of mass 59, the others being 57 and 58 respectively. It looks as if the iron isotope of mass 56 is responsible for the high magnetisability of iron.

The regularity of odd and even valencies associated with odd- and even-number isotopes seems to break down at nickel and cobalt.

The calculated atomic-weights of nickel and iron when averaged become equal to the average of the experimental values, suggesting thereby a certain amount of perhaps unavoidable contamination in the experimental determinations.

From a study of the values obtained by the method of positive rays and these relations, I have come to the conclusion that further experimental work on isotopes may reveal the fact that, under certain conditions of extreme dilution, it will be possible to get "mass spectra" of many metallic elements. Moreover, that some of the atoms may be broken up so that the values recorded are not always representative of those functioning in ordinary chemical actions, or in ordinary physical processes. There is also the possibility of a small percentage of contamination due to what might be termed broken or disintegrated atoms—not necessarily due to radio-activity. This may account for the masses obtained by chemical methods deviating from the theoretical values; but, on the whole, the values seem very concordant: probably they are, for the most part, within the range of experimental error.

There is a regularity in the extended table which points to the possible modification of the nitrogen outlier, in that it may consist of two α -parts taken together instead of one more "compact" β -part; but as Sir E. Rutherford lays stress on the disrupted member of nitrogen having possibly a mass of 2 (see CHEMICAL NEWS, 1919, cxviii., p. 311), such evidence would appear possibly to contradict experiment. I am, however, aware that further experiments have been made which may clear up the difficulty. In the absence of full details of such experiments, this point cannot be discussed from the experimental side.

An attempt to explain the non-isotopic characteristic of C, N, O, and F has already been made (see CHEMICAL NEWS, 1915, cxi., p. 157), but there may be a further peculiarity as a contributory cause. These particula-

elements may be made up of sub-atoms of masses indicated by n in the table on p. 183, and the number (n) may be 4 in each case.

EQUATION OF STATE.

By FRED. G. EDWARDS.

THE equation of molecular heat, namely, $k = m \cdot x \log T$, may be converted into the equation of state $b(k + a \log \theta) = m \cdot x \log T$, where θ is the number of degrees below the critical temperature, a is an infinitesimal coefficient producing the relative values of the intrinsic pressures at the critical and observation temperatures respectively, and b is a constant making the sum in brackets equal to the intrinsic pressure, the surface tension, or the volume density, with any given units. The values of y obtained from $m = 5.95/y$ and $m = 4 - (2y/2.95)$ will give the specific heats at variable volume, while m will be integral at the natural temperature of change of phase and recalcrescence. The specific density ratio $D = A m \cdot x \log T$, and the coefficient of linear expansion—

$$d.V/3d.T = \frac{1}{3} d.I/A m \cdot x \log T = T/3 A m \cdot x.$$

The atomic volume ratio $V = 1/m \cdot x \log T$ is a more general form of the equation of Lotzner Meyer's curve $V = A/D$. The tangent to the curve $d.V/d.T = T/m \cdot x$, and the minimum values $d^2.V/d.T^2 = m \cdot x = 0$. Also, $d.D/d.T = A m \cdot x/T$. The datum value of k will vary for each change of phase with the intrinsic pressure. The values of x are 0.0698 A $\frac{1}{2}$ generally, for certain gaseous substances 0.76384 A $\frac{1}{2}$, and for hydrogen, unity. It will be found that Groups V. and VI. of the Periodic Table form one homogeneous group as required for symmetrical atomic shape built up from a primordial mass unit, which may be nebulium. The coefficients of these equations can only be determined by a very extended analysis of the physical state of liquid and solid substances; but inspection shows that the terms are of the right order of magnitude, and, moreover, they are derived from an equation showing exact agreement with the specific heat at constant volume, and there is a distinct parallelism between the coefficient of expansion and the specific heat at variable volume.

THE EXAMINATION OF CHINESE CRUDE CAMPHOR.

By E. R. DOVEY, A.R.C.Sc., A.I.C.,
Government Laboratory, Hongkong.

In the examination of crude camphor, the estimations usually required are those of non-volatile matter (or dirt), moisture, and oil, and the sum of these impurities subtracted from 100 per cent is supposed to represent the camphor present. The moisture may be conveniently estimated by the calcium carbide method, allowing three hours for the evolution of gas, and the dirt by the residue left after volatilising a weighed portion of camphor.

So far as is known to the writer, no reliable method for the estimation of camphor oil in crude camphor has been published, other than the melting-point method given in Allen's "Commercial Organic Analysis," vol. iv., p. 197.

As this laboratory was called upon to examine a considerable number of Chinese crude camphors, the following method worked out here may be of interest:—The moisture is first estimated on the well-mixed sample, then 100 grms., weighed to the nearest 0.1 gm., are transferred to a press and pressed between two layers of lint. The press designed for this work has a steel cylinder 2 inches in diameter and 6 inches deep, and is furnished with a movable perforated bottom plate. The piston is operated by a strong screw thread. The sample is allowed to remain in the press under pressure for fifteen

minutes, at the end of which time it is carefully removed and the pressed cake weighed, any camphor adhering to the lint being carefully brushed off and added to the cake. From the loss in weight the amount of water plus oil expressed is found.

The moisture is then estimated on the pressed cake, and from the difference between the result and the original moisture the amount of water expressed is found, and, by difference, the amount of oil in the expressed liquid is found.

It is then assumed that the water still remaining in the pressed cake is associated with as much oil as that in the expressed liquid, and the total oil calculated on that basis. The accuracy of this assumption may be open to question, but, with a good press, very little moisture remains in the cake, while the m. pt. of the pressed camphor usually indicates a fairly high degree of purity.—*The Analyst*, June, 1920.

DETECTION OF MINUTE QUANTITIES OF PETROLEUM SPIRIT IN VEGETABLE OILS.

By MASASHIRO AIDA.

A NUMBER of methods for the detection of petroleum spirit in vegetable oils have been proposed. A careful study of these has shown that they are not satisfactory, but it has been found that Nastjukoff's formolite reaction may be applied successfully for the purpose as follows:—

The oil (50–100 grms.) is saponified by means of potassium hydroxide solution. Distilled water and pure calcium chloride solution are added, the liquid distilled by means of steam, and the distillate treated with 40 per cent formaldehyde solution and a few drops of concentrated sulphuric acid. A reddish brown film coloration on the surface of the liquid, gradually changing to deep yellow, indicates presence of petroleum spirit. If a few drops of the distillate are added to water, a brilliant interference ring of optical waves is produced on the surface of the water; this ring becomes almost invisible after standing for some time and disappears completely on heating. With soya bean oil the ring does not change, even on heating. The above process is capable of detecting traces of petroleum spirit in vegetable oils, and may be made the basis of a quantitative method, the formolite precipitate being weighed after drying at 110–115° C.—*Journal Society Chemical Industry*, June 15, 1920.

A REVISION OF THE ATOMIC WEIGHT OF TIN.*

By HENRY KREPELKA.

WE have determined in a new and more careful series of trials the ratio $\text{SnBr}_4 : \text{Ag}$ by analysis of newly prepared tetrabromide of tin.

The materials for this purpose were prepared with great care and cleanliness, and chief attention was paid to removing all traces of moisture from the bromine used for the synthesis of the tetrabromide, and to keeping the latter in an absolutely dry state. Individual analyses were carried out in the same way as before (B. Brauner and H. Krepelka (*Ann. Chem. Soc.*, xlii., No. 5), although one profited, of course, by the experience gained in the earlier work. The details follow.

Preparation of New Materials.

(The remaining reagents not mentioned here were prepared in the same way as stated in the preliminary work).

Bromine.—Ordinary bromine was shaken in portions in a separatory funnel containing distilled water, every

* Presented to the Bohemian Academy of Sciences, Prague, 1919. From the *Journal of the American Chemical Society*, xlii., No. 5.

No. of analysis.	No. of bulb.	SnBr ₄ . Grms.	Corr. for vacuum. Grms.	Silver corr. for vacuum. Grms.	SnBr ₄ :4Ag.	At. wt.	Differences from the mean.
1.	19	5.11681	5.11788	5.03796	1.01586	118.702	0.003
2.	8	2.46823	2.46875	2.43035	1.01587	118.674	+0.025
3.	9	0.99489	0.99510	0.97961	1.01581	118.679	+0.020
4.	18	1.69798	1.69834	1.67172	1.01592	118.727	-0.028
5.	21	3.54191	3.54265	3.48737	1.01585	118.697	+0.002
6.	15	3.82100	3.82180	3.76199	1.01590	118.717	-0.016
Mean					1.01586	118.699	=0.018
					Maximum =	118.727	
					Minimum =	118.674	
					Difference =	0.053	

portion being thus treated three times. This bromine was then redistilled from a saturated solution of potassium bromide. The distillate was allowed to drip into a solution of potassium oxalate prepared by neutralising pure oxalic acid with pure potassium carbonate. The potassium bromide thus obtained was recrystallised three times, and its solution was evaporated with a small quantity of potassium dichromate and twice distilled sulphuric acid. The bromine thus set free removed all iodine that may have been present. This evaporation was repeated three times. In order to remove organic matter the dry bromine was melted in small quantities in a platinum crucible. From this remelted bromine bromine was set free by means of an amount of potassium dichromate and sulphuric acid, such as to leave undecomposed bromine in the distilling flask. The bromine was then redistilled, and from a portion of this distillate was prepared the calcium bromide used to dry the remaining part of the bromine, which was then further dried by shaking it with phosphorus pentoxide (twice sublimed in a stream of oxygen), and was afterwards distilled directly into the apparatus in which the synthesis of tetrabromide took place.

Tetrabromide of tin was prepared in the modified Lorenz apparatus. During the preparation the communication with the outside air was effected by a drying system (described in a previous communication—*Journ. Am. Chem. Soc.*, xlii., No. 5, p. 917) to which were added tubes containing sublimed phosphorus pentoxide.

The course of the reaction showed that both the bromine used and atmosphere of the reaction bottle were absolutely free from moisture, since the first drop of bromine did not at once react with the tin-foil—only after five minutes did the reaction begin slowly to take place. As soon as the first foil was covered with tetrabromide the reaction became violent and accompanied by such heat that the surrounding pieces of foil were melted into a ball, and the whole reaction bottle had to be quickly cooled.

The tetrabromide obtained was introduced into glass bulbs provided with cone-shaped necks and there sealed. This arrangement removed the difficulties encountered at the same operation during the preliminary work, when the bulbs used had straight necks.

Silver.—750 grms. of pure ordinary silver was dissolved in portions in distilled nitric acid (1:2) in such a way as to leave a small part of the silver undissolved.

The solution of silver nitrate thus obtained was heated to the boiling-point, and, after the expulsion of nitrous gases, was filtered. The clear solution, coloured pale blue by copper, was allowed to crystallise by evaporation. Silver nitrate thus obtained was fused in a porcelain dish until the melted mass became black. This black substance was dissolved in water, and the solution was filtered and allowed to crystallise by evaporation. The crystallisation was repeated three times. A spectroscopic examination of the last crystals showed only the lead line 3683.62 (intensity 1000), proving thus that all other metals had been removed.

The silver nitrate obtained in this manner was reduced by ammonium formate (prepared from pure formic acid and freshly distilled ammonia) and the reduced silver was washed with distilled water until the Nessler reagent gave no test for ammonia, dried in an electric drying oven at 150°, and then melted in a current of pure hydrogen according to the method elaborated by T. W. Richards (*Journ. Am. Chem. Soc.*, 1905, xxvii., 472).

Pure hydrogen for this purpose was obtained by the electrolysis of a solution of pure sodium hydroxide prepared from pure metallic sodium. The apparatus used consisted of a long U-shaped tube, in one arm of which was evolved oxygen and in the other hydrogen. The arms were long in order to prevent the mixing of the two gases. The hydrogen was conducted into a purifying system composed of two Richards' washing flasks filled with a saturated solution of silver sulphate, a U-tube containing fused sodium hydroxide, a tube filled with red-hot pumice stone covered with platinum and of another U-tube containing fused sodium hydroxide. The individual parts of the apparatus were connected by means of airtight ground joints.

Grains of remelted silver were etched with dilute nitric acid which had been redistilled, then washed successively in distilled water, ammonia water, and again in distilled water.

The final delicate operation, namely, the preparation of small pieces of pure silver for weighing, was carried out in the following manner:—The greater portion of the silver buttons was cut up into small pieces on a slab of pure silver with a sharp steel chisel—the pieces were then etched and washed as above. The remaining grains were rolled between clean steel rollers in such a way that after each passing through the roller the silver was etched and washed in order to remove any trace of iron which it might have acquired. The silver foil was then cut by scissors into small pieces, which were then etched and washed as before.

Weighing was done on the same balance as in the preliminary work, but not until after the weights had been tested and corrected.

Six analyses were made in this series, and the results are given in the accompanying table.

Discussion.—The mean value from six determinations is 118.699 (± 0.016). The maximum figure, 118.727, found only once, was arrived at by the analysis of Bulb No. 18, which was filled as far as to the neck. The minimum was 118.674, and this was the result of the analysis of Bulb No. 8, likewise filled up to the neck. The maximum difference between the highest and lowest values is thus 0.053. The mean value of all six ratios, SnBr₄:4Ag, is 1.01586. The only probable source of error of this series of analyses appears to have been the space in the necks of the bulbs not filled with tetrabromide.

The agreement of the resulting mean value of the atomic weight of this series of analyses with the mean value of the preliminary determination increases the probability of this figure, and supports the value of the atomic weight of tin,

118.699 (118.70), as determined by Briscoe (*Journ. Chem. Soc.*, 1915, cvii., 76), and by Baxter and Starkweather (*Proc. Nat. Acad. Sci.*, 1916, ii., 718). This value has been accepted by the International Committee on Atomic Weights.

In conclusion, I wish to express my gratitude to the Bohemian Academy of Arts and Sciences in Prague, with whose financial support this work was carried out. I am also obliged to Professors Dr. B. Brauner and Dr. Sterba-Böhm for their valuable advice as well as to Dr. Sveda for his kind assistance.

THE ATOMIC WEIGHT OF LEAD FROM A JAPANESE RADIO-ACTIVE MINERAL.

By THEODORE W. RICHARDS
and
JITSUSABURO SAMESHIMA.

THE lead used in this work came from Hokuto, Formosa, Japan, and was separated from a crystalline mineral crust containing lead and barium which had been formed in the bottom of a hot spring (Okamoto, *Beitr. Mineral. Japan*, 1912, iv., 178). According to Hayakawa and Nakano this mixture of minerals contains (besides cerium and lanthanum) some radio-active elements, namely, ionium, polonium, and radium, but no uranium (Okamoto, *Journ. Geol. Soc. Tokyo*, 1911, xviii., 19; Hayakawa and Nakano, *Zeit. Anorg. Chem.*, 1912, lxxviii., 183). With their apparatus, however, they were unable to discover radio-activity in the lead chloride obtained from it.

About 10 grms. of metallic lead obtained from this specimen was dissolved in pure nitric acid, and the lead nitrate was recrystallised several times and then converted into chloride by freshly distilled pure hydrochloric acid. The lead chloride was recrystallised four times by dissolving the crystals in hot water in a quartz dish and adding hydrochloric acid. Before the last crystallisation the hot solution of chloride was filtered through a Gooch-Munroe crucible. Owing to the small amount of material no further purification was attempted. This lead chloride was then used for the determination of the atomic weight of lead.

The ordinary lead used for comparison was obtained from lead acetate, converted into chloride, and recrystallised five times in the same manner as the Japanese lead.

The method of analysis was similar to that often described in other papers (Baxter and Wilson, *Proc. Am. Acad.*, 1907, xliii., 363; Richards and Lambert *Journ. Am. Chem. Soc.*, 1914, xxxvi., 1335; Richards and Wadsworth, *Ibid.*, 1916, xxxviii., 2613; Richards and Hall, *Ibid.*, 1917, xxxix., 536). Moist crystals of lead chloride (after washing the last crop with pure water) were transferred directly into a platinum boat which had been previously weighed. By this procedure handling and danger of accidental introduction of dust were minimised. The boat was kept in a desiccator until the crystals were dry, then brought into the tube of the "bottling apparatus," fused in a current of pure dry hydrogen chloride and weighed. The salt was dissolved in water containing a drop of pure nitric acid, and no black insoluble residue remained suspended in the solution.

The chlorine contained in this solution was precipitated in the usual manner by its approximately calculated equivalent of silver. The attainment of the exact equivalence between the silver and the chlorine was effected by the addition of one or the other and tested in the nephelometer in the customary way.

All the weighings were reduced to the vacuum standard, the correction for which was calculated from the density of the substances and that of the brass weights. All precautions used in this sort of work were maintained.

Because of the small amount of the material, the same specimen of Japanese lead salt was used in each analysis.

After the first determination was finished, a slight excess of hydrochloric acid was added to the filtrate from the silver chloride in order to remove the last traces of silver; and the supernatant liquid was filtered, evaporated in a quartz dish to small volume and filtered again. This solution was mixed with the purest mother liquor from which the previously used crystals of lead chloride had been deposited, and evaporation was continued until most of the chloride was deposited as crystals. The product was recrystallised from hot water, and then used for the second determination of the atomic weight. A similar treatment intervened between the second and third experiments. One analysis, being defective in execution, was rejected. The parallel determinations made with ordinary lead show that the details of procedure had been adequate, since the result agrees sufficiently well with the more extended and elaborate work of others.

The results obtained are given in Table I. (The atomic weights of silver and chlorine being taken as 107.88 and 35.46, respectively):—

TABLE I.—The Atomic Weight of Lead.
(From the ratio, 2Ag : PbCl₂).

Corrected wt. of fused PbCl ₂	Corrected wt. equivalent Ag.	Ratio PbCl ₂ : Ag.	Atomic weight.
Ordinary lead—			
3.13929	2.43553	1.28895	207.185
3.09476	1.40100	1.28894	207.183
Average..			207.184
Japanese lead, first determination—			
2.16756	1.18212	1.28859	207.11
1.14536	0.88881	1.28864	207.12
1.34496	1.04358	1.28879	207.15
Average..			207.13

The fact that the latter three analyses show a progressive increase in the value of the atomic weight suggests the possibility that the degree of purity of the three preparations might have progressively changed. Nevertheless, since from the method of crystallisation they should have been essentially alike, the appearance of a march in the figures is probably fortuitous. In any case no claim can be made for great accuracy in the result, because the amount of crude material was not sufficient for work of the highest precision. In spite of this lack, the outcome serves its purpose, for it shows that the atomic weight of this lead from a Japanese radioactive spring is not far from that of ordinary lead. Probably it is chiefly ordinary lead, with perhaps not over 5 per cent of isotope of lower atomic weight. The result coincides well with the fact, reported by Hayakawa and Nakano (*loc. cit.*), that the lead chloride shows but little if any radioactivity. The quantity of the metallic lead obtained was too small to determine a trustworthy value for its density.—*Journal of the American Chemical Society*, xlii., No. 5.

NEW PROCESS FOR VULCANISING RUBBER.

THE rise of the rubber industry, which was founded in Manchester by Macintosh in 1825, to its present position and magnitude may be directly attributed to the discovery by Goodyear, in 1839, of the process known as vulcanisation. Raw rubber, which Macintosh employed in the earliest days as a proofing for fabrics, is by no means a suitable material from the manufacturer's point of view, for the production of a finished article, in spite of the fact that it possesses a number of unique properties.

Amongst other drawbacks to its use are the facts that it is strongly adhesive, and that it is sensitive to changes of temperature, becoming soft and tacky at a summer

heat and stiff and hard in the winter. These defects alone would have sufficed to limit very seriously its uses in industry. In fact, it is safe to say that but for Goodyear's investigations and subsequent discovery, the industry would have been one of minor importance if indeed it had continued to exist at all.

Goodyear found that by incorporating rubber with sulphur and heating for a suitable period to a temperature of about 140 deg. Cen., rubber becomes profoundly modified and acquires new properties which render it eminently suitable for the manufacture of a host of useful articles. It loses its adhesiveness, becomes resistant to temperature changes, and exhibits greatly enhanced strength, elasticity, and durability. A year or two later Hancock, in England, independently discovered the process, his method consisting in immersing sheets or formed articles made from raw rubber in a bath of molten sulphur at a temperature of 135–140 deg. Cen. In principle the two methods are the same.

In 1846 Parkes showed that rubber could be superficially vulcanised by immersing it in a cold dilute solution of sulphur chloride in carbon bisulphide. This method is adapted to the vulcanisation of thin sheets or films of rubber only.

From these early days up to the present time all manufactured rubber goods have been vulcanised by one or other of these three processes, that of Goodyear finding by far the widest application.

An entirely new process for effecting vulcanisation has recently become available as the result of the discovery, by Mr. S. J. Peachey, Lecturer in Chemistry at the Manchester College of Technology, that by exposing rubber alternately to the action of two gases, viz., sulphur dioxide and hydrogen sulphide, it becomes rapidly and completely vulcanised, even at the ordinary temperature. The process appears to be of fundamental importance for the following reasons:—

1. It is a true sulphur vulcanisation (as distinct from the sulphur chloride treatment) and yields a product entirely comparable with that obtained by the Goodyear process.
2. It eliminates the use of heat, and to a great extent the use of mechanical pressure.
3. It employs two gases, both of which can be produced on the large scale at a very cheap rate.
4. It is rapid in action.
5. It enables the manufacturer to employ organic filling agents such as leather waste, sawdust, shoddy waste, and the like, which cannot be used in connection with the hot process. In this manner a number of cheap and highly-durable materials may be fabricated from the various wastes, and employed as floor and wall coverings, for boot and shoe manufacture, and for upholstery work.
6. Coal-tar dyestuffs and even natural dyes, which, with a few exceptions, are destroyed by the "hot cure," can be introduced into mixings to be cured by the new process with the production of delicate tints and shades hitherto unobtainable.

The process has the advantage of extreme simplicity, and its translation from the laboratory to the works should prove a very simple matter.

Already numerous samples of daintily coloured floor coverings, fancy leathers, and felts, suitable for hat making, have been produced in the laboratory, and these have an appearance and a finish which could hardly be improved upon. Several pairs of boots have been soled with leather reformed from waste by the new process, and the practical test of several months' hard wear has shown that the reformed leather is even more durable than the real article.

The process can be extended to the vulcanisation of rubber in solution. If a solution of rubber in benzole or naphtha be saturated or partly saturated with hydrogen sulphide and mixed with a solution of sulphur dioxide in

the same solvent, the liquid sets in a few moments to a stiff jelly, and on eliminating the solvent by evaporation a fully vulcanised rubber is obtained. The use of the mixed solutions for producing perfectly vulcanised seams and joints has proved highly satisfactory in practice, and inner tubes repaired in a few moments by the new process have an excellent life. Further, by the aid of the solution process, reformed leather soles and heels may be attached to boots without the aid of stitching or nailing, and indeed a boot may be produced from the reformed leather without a single stitch being necessary.

The above-mentioned applications of the process have been fully worked out in the laboratory, but they do not exhaust a fraction of its possibilities—and new technical effects in many other directions are continually presenting themselves.

The Peachey Process is fully protected all over the world.

TUNGSTEN MINING IN CHINA.

The discovery of tungsten in China occurred in recent years, the deposits being found in the southern provinces, below the 30th degree of north latitude. At the present time, with a few exceptions, the mines are not owned by any private companies or by the Government, but any one may employ men to work a mine.

From a report by the United States Vice-Consul at Shanghai, it appears that the principal districts in which tungsten is found are in the Provinces of Hunan (southern part), in Hangchow and its vicinity; Kiangsi (southern part), in the Lungnanhsien, Tinnan, Singfenghsien, Nankanghsien, and Taiyu districts; and Kwangtung (eastern part), in the Wuwha, Hingninghsien, Kaiyung, Heifung, Luklung, and Wallia districts (northern part), in the Namyung, Lokchong, Chibing, and Chukiang districts. The districts mentioned above are only those in which operations are now being carried on, there being other large areas in which tungsten deposits are found, in the southern parts of the Provinces of Hunan and Kiangsi and the north-eastern part of Kwangtung, which have not as yet been opened.

Chinese tungsten, in the form of wolframite, occurs either as sand or pebbles in the streams or in small veins in the granitic rocks. The former deposits are sometimes accompanied by cassiterite or magnetite, or both, usually mixed with quartz sands, the latter in the form of veins ranging in thickness from a fraction of an inch to 2 or 3 inches. Although both kinds of deposits are found in many widely scattered regions, they are never found in large quantities in any particular area. For this reason, and also because this industry is of very recent origin in China, no modern systematic methods have been inaugurated to explore this field.

Rakes, toms, and pans are used for washing the stream ores, while in the case of vein ores, hand hammers, drills, and sometimes black powder are used for extracting the valuable contents of the ore. With the exception of a few places in Hunan and Kwangtung, nearly all the mining is carried on by farmers, who work during their spare time after their farming labour is completed. But during the early part of 1918 the industry had grown to such an extent that many of the farmers suspended their farm work and devoted themselves entirely to tungsten mining.

The concentrates offered on the market are rather impure, and usually have to be reconcentrated for export purposes. For this purpose a few native as well as foreign companies have sprung up, each having a concentrating plant of some sort. One concern has a fairly well-equipped plant, containing shaking screens, jigs, rocking tables, and round revolving tables for concentrating its own ores and those collected from mining centres; and it is in a position to produce concentrates of

67-72 per cent WO_3 with about 5 per cent of manganese, and containing but a small amount of impurities, such as copper or tin.

The farmers take their concentrates to the local market, where they dispose of them to local dealers at the best prices obtainable. The local dealers, in turn, sell them to licensed collectors from the ports. The port dealer has to pay a tax to the Government, and, after shipping the concentrates to his own port, he is under obligation to export them within a certain period, usually three months. If he fails to do this he is obliged to get another licence for the same ore or forfeit the ore to the Government.

The total exports of tungsten ore in 1918 amounted to 10,365 tons (of 2000 lbs.), but the total production during the year far exceeded this figure, there being large quantities left in the mining districts which could not be sold owing to the cessation of hostilities in Europe. The working of the deposits continued, nevertheless, until February, 1919, when it was found that the returns would not cover the cost of labour.

Up to August, 1919, tungsten ore was wholly an export product, as China had no way of utilising the ore. A plan was formulated for establishing a plant at Hankow for making ferro-tungsten, but the scheme was postponed on account of the inactivity of the tungsten market. It is understood that there is a small smelting plant at Dalny, which, however, is still in an experimental stage.

It is difficult, adds the United States Vice-Consul, even to estimate approximately the quantities of future production for any definite length of time, as, thus far, no authoritative survey has been made of this field in China. It is estimated that all the mines in the above-mentioned districts are capable of equalling their production during the year 1918 for more than ten years. Future shipments abroad will be governed entirely by the demands of the American and European markets.—*Journal of the Royal Society of Arts*, June 18, 1920.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 17, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE CROONIAN LECTURE was delivered by Prof. WILLIAM BATESON, F.R.S., on "*Genetic Segregation*," of which the following is a summary:—

Later developments of genetics have been, in the main, attempts to discover the nature and scope of *Segregation*. Mendel proved that certain characters are determined by unit-factors. Their integrity is maintained by segregation—the capacity, namely, to separate unimpaired after combination with their opposites. We have been trying first to ascertain specifically what characters behave in this way; whether there is any limit to the scope of segregation, or any classes of characters otherwise transmitted. Among characters known to be subject to segregation are illustrations of most of the features by which plants and animals are distinguished. In regard to two classes of characters the evidence for segregation is, nevertheless, rather noticeably imperfect. No quite clear proof exists that differences in number, *meristic* characters in the strict sense, are governed by segregable factors. The extra toe of the fowl and the single leaflet of the monophyllous strawberry are perhaps the best examples, but reservations may be entertained. Also, though segregation can be demonstrated in regard to *quantitative* characters, parental types thus distinguished often fail to reappear and the inheritance is subject to special complications.

Groups or complexes of factors are now recognised as sometimes segregating whole. Were it not that on occasion elements of the complex become independent, the group would pass for one unit factor. The sex-com-

plex is an obvious example. Intermediate flower-colours like those of modern sweet peas arise by this process. In peas, colour in flowers and axils may behave as one unit, but the axillary element may drop out. The plausible suggestion that the new terms are only rare cross-overs in a closely linked series does not fit the evidence. A striking illustration appears in *Oenothera*, in which, as Renner lately showed, several groups of characters normally segregate as single factors. These complexes are in several forms not borne equally by the two sexes of the plant, and most of them cannot exist in the homozygous state. By these discoveries the *Oenothera* problem is greatly elucidated.

The second question is to determine when in the life-cycles segregation can occur. Admittedly it is a phenomenon of cell-division. If we knew the animals only we might confidently adopt the view of Morgan that normal segregation happens during the maturation process at the stage of synapsis, when the maternal and paternal chromosomes are believed to conjugate in pairs. Most of the facts of linkage may be thus well represented, but the absence of crossing-over in the sex-heterozygote (*Drosophila* and silkworm) is not readily explicable, nor is there as yet extensive evidence that the number of linkage-systems agrees with that of the chromosomes—a primary postulate of Morgan's theory.

The evidence for an orderly anastomosis, or even of any exchange of materials between chromosomes is weak, and the visible features of chromosomes are scarcely suggestive of the prodigious heterogeneity requisite. Even if the linkage-systems correspond with the chromosomes, which is a most attractive conjecture, exchange of material between chromosomes need not be essential to crossing-over. It may be doubted, however, whether the general course of cytological evidence does not point to the rôle of the chromosomes being rather passive than active.

That in plants segregation, even in its normal course, is not limited to the reduction-division is now certain. In *Matthiola*, *Campanula*, *Begonia*, and *Oenothera*, the genetic composition of the male and female organs may be normally different, and segregation cannot have happened later than the constitution of these organs. Collins's evidence from *Funaria* proves further that sex-segregation may happen during the growth of a haploid form.

Periclinal chimeras and the production of distinct types from adventitious buds prove that segregation may take place during embryonic development, whether in the differentiation of the layers or of the root. In the genetic properties of the tare-like rogues of peas there are features which illustrate not only the occurrence of gradational change in genetic properties following somatic differentiation, but also that this gradation affects the male and female organs differently. From these facts it must be concluded that normal and orderly segregation (apart from chance sporting) can occur at various cell-divisions, and not exclusively at reduction. Not improbably these somatic segregations may be accompanied by some visible cytological differentiation, but that question must not be prejudged.

Having regard to the fundamental distinctions between the morphological relations of the germ cells to the soma in animals and in the flowering plants, it is not surprising that the processes of segregation should be differently effected in these two groups of organisms.

PHYSICAL SOCIETY.

Ordinary Meeting, June 11, 1920.

W. R. COOPER, Esq., in the Chair.

THE CHAIRMAN announced, with regret, that a telegram had been received intimating the death of Prof. Aug. Righi, of the University of Bologna, one of the Honorary Fellows of the Society.

A paper entitled "*Radiation and Convection from Heated Surfaces*," by Dr. T. BARRATT and Mr. A. J. SCOTT, was read by Dr. Barratt.

The relative and absolute amounts of radiation and convection from surfaces heated to about 100° C. in air were measured as follows: steam was passed through the cylinders or spheres, the surface temperature being measured by a thermo-junction. The total amount of heat lost from the surface was determined from the equivalent mass of steam condensed. This was done with the surface (a) "bright," (b) "dead-black." The relative amounts of radiation alone from these two surfaces were then found with the aid of a thermopile. If h_1 is the total heat lost, and r_1 the radiation, per square centimetre per second per 1° C. excess of temperature for the "black" surface; h_2 and r_2 corresponding quantities for the "bright" surface; and c the convection in each case, then if $h_1 = ah_2$, $r = br_2$,

$$\frac{r_2}{h_2} = \frac{a}{b-1}, \quad \frac{r_1}{h_1} = \frac{b(a-1)}{a(b-1)}.$$

The numerical values of the radiation, convection, and total heat are then easily calculable, and are given in tables. It is found that the amount of convection per square centimetre is inversely proportional to the square root of the diameter of a cylinder, and to the cube root of the diameter of a sphere.

DISCUSSION.

Mr. C. R. DARLING pointed out that the numerical results contained some considerable discrepancies. For instance, in Table 2, for an excess of 75.6° the heat loss was 2869 units, while with a higher temperature excess of 80.2° it was only 2780. Something must be wrong, and he distrusted the use of steam condensation methods of measuring the heat lost. Water traps were never satisfactory. Why not use electrical heating? A second point was the method of measuring the surface temperature by inserting a thermo junction in a little notch. Some experiments he had once made showed that the conditions just under the surface differed considerably from those at the actual surface when heat escaping. Had the author tested the results mentioned by Langmuir (*Journ. Am. Electro-Chem. Soc.*, vol. xxiii., 1913)? Langmuir states that the convection loss is equal to the heat conducted through a layer of air of particular thickness surrounding the hot body. Further, the loss from a plane disc is 10 per cent more when the disc is horizontal than when it is vertical. In the horizontal case the loss from the lower surfaces is 50 per cent less than from the upper. Langmuir found that the phenomena of natural convection did not agree with Russell's formulæ, but forced convection did.

Dr. ELZER GRIFFITHS thought the paper of interest inasmuch that it contributed some data for cylinders of moderate diameters and for spheres. The experimental work of Langmuir referred to by the last speaker did not cover the same ground, since it dealt only with fine wires and one flat surface. He agreed that the method of steam heating was not altogether satisfactory, although most of the data relating to steam pipes had been obtained by means of it. When electrical methods were employed the difficulty was the large amount of energy which had to be supplied. For example, in some experiments on convection loss now in progress it was necessary to supply about 18 kw. of electrical energy to heat up a cylinder 9 in. in diameter by about 4 ft. long to a temperature of about 450° C. He did not think that the experiments of Dr. Barratt proved conclusively the relation between diameter and convection loss per unit area given in the paper. It was a well known fact that the change of heat loss with diameter was greatest with cylinders of small diameter, such as wires, but above about 3 in. in diameter the change was small and the form of the curve connecting heat loss (convection per unit area), and diameter for the complete range of diameters (wires of 2 mils to cylinders 9 in. diameter), was of the form which he illustrated on the board.

Capt. DUNSHEATH said that at present millions of pounds were invested in cables for conveying electric power, and more information on the heat loss from such cables would be of the greatest practical value in determining the necessary thickness of copper to employ. The present experiments, however, did not carry us far in this respect, as the cable is rarely suspended in free air. It would be useful if the experiments could be carried out with the cylinder in contact with a plane or lying in a duct. As regards the measurement of surface temperature, he thought the conduction along the wires of the couple would affect this unless they were arranged to be in thermal contact with the surface for some distance from the junction. How was the effects of draughts eliminated? Were any steps taken to measure the air currents existing before the cylinders were heated?

Mr. G. D. WEST mentioned the importance of the inclination of the surfaces to the vertical. With wires in tubes a great deal depended on whether the tubes are horizontal or vertical. If the author could give us data on this point, we should be a step nearer measuring the conductivity of the surrounding gas, which, at low pressures, is more important than convection.

Mr. F. E. SMITH agreed with what had been said regarding the inefficiency of steam traps. It appeared to him that measurements of this type could be carried out by using very thin walled tubes conveying an electric current. By measuring the resistance of the tube, both the temperature and the energy consumed could be determined.

Dr. BARRETT said he would prefer, as time was short, to communicate a reply to the points raised by the various speakers.

A paper on "*An Electrical Hot-Wire Inclinator*" was read by Mr. J. S. G. THOMAS.

The hot-wire inclinometer consists essentially of two fine platinum wires (diameter about 0.1 mm.) mounted parallel to one another in a closed chamber at a distance apart equal to about 1 mm. A constant current of from 0.4 to 1.5 ampere (according to the sensitivity desired) is maintained in the wires, which constitute two of the arms of a Wheatstone bridge arranged so that the bridge is balanced in the zero position of the inclinometer. If desired, the bridge may be constituted of two pairs of heated wires as above. The inclinometer wires, in the zero position, may be either vertical or horizontal or inclined at any angle to the horizontal. The indications of the instrument are dependent upon the relative heating or cooling effects experienced by the respective wires when the orientation of the wires about a horizontal axis is altered. The galvanometer deflection occurring with alteration in such orientation serves to indicate the inclination of a definite radius vector to the horizontal, and calibration curves are given for the cases where the axis of rotation is horizontal, and (a) in the plane of the wires and parallel to the wires, and (b) at right angles to the plane of the wires. The characteristics of the calibration curves are discussed and curves are given showing how the resistances of the respective wires depend upon the orientation of the wires. Attention is directed to the finite width of the column of heated gas ascending from the wires, and an empirical formula is deduced expressing the maximum deflection as a function of the bridge current employed.

DISCUSSION.

Dr. BARRATT mentioned that in a previous paper Mr. Thomas had attributed certain effects to radiation between wires separated by about 100 times their diameter. He (the speaker) had pointed out that such an effect would be entirely negligible; and he was glad to see that the author had discarded radiation in the present paper.

Mr. GOSLING said that Mr. Thomas's apparatus seemed excellent for exploring the temperature in the convection stream both above and below a hot wire. He was not clear whether Mr. Thomas assumed that the narrow column of rapidly moving air extended to an equal extent

below the hot wire. It would be interesting to establish if this were the case. Another interesting point was the connection, if any, between the central core of the hot column and the total width. When a hot body is standing in air there is a very definite zone of hot gas surrounding it. He had observed this recently by Zoepler's "schlieren" method (which he described), but it was not possible to say from the appearance of the currents above a candle-flame, for instance, whether an actual discontinuity existed at the edge of the current or not.

Mr. J. GUILD pointed out that these and other points could readily be investigated quantitatively by placing the apparatus in one beam of a Michelson interferometer arranged to give "Contour" fringes.

Mr. F. J. W. WHIPPLE referred to the practical applications such as the use of the instrument in an aeroplane. How would the results be effected by angular acceleration of the system?

Mr. F. E. SMITH emphasised this point. It appeared that this inclinometer would give precisely the same indication as a mechanical inclinometer, such, for instance, as a suspended bob or a marble in a glass cylinder. In the two possible cases of unaccelerated flight, viz., right way up and upside down, there was never any doubt.

Dr. BARLOW asked if the pressure of the gas affected the results given by the instrument?

Dr. HOPWOOD asked how the behaviour varied with the diameter of wire used? Some time ago he had heated two loops of fine wire in series in coal gas. At atmospheric pressure the finer of the two glowed perceptibly and the other did not. On reducing the pressure it was possible to get the thicker wire glowing while the other was dark. Could any anomalous effects arise from such causes as this?

Mr. THOMAS, in reply, said that in a previous paper he had determined the ratio of the thermal conductivity of various gases to that of air. He had found the same ratio at 600° C. as at ordinary temperatures. He had interpreted this as indicating the existence of a skin of occluded gas round the wire. The thickness of this skin would be the b term in King's formula. He had not yet investigated the conditions below the wire. Mr. Guild's suggestion of doing this with an interferometer was very interesting. With regard to Mr. Smith's remarks he agreed that the instrument only indicated the apparent direction of gravity, but he had had the impression that there was some difficulty in discriminating between right and wrong way up in certain cases, and that there was no satisfactory indicator for this purpose in use. Another application connected with aviation is in setting the nose of experimental models exactly head on to the wind. Experiments had been made with various wires and no anomalies of the type mentioned by Dr. Hopwood were found. The gas was at atmospheric pressure in practice.

A paper on "Convective Cooling and the Theory of Dimensions," was read by Mr. L. F. RICHARDSON.

The paper consists of an application of the "Principle of Similitude" (Rayleigh, *Nature*, 1915, xcv., 66) to the loss of heat from hot wires, thermometer bulbs, &c. An equation is obtained which does not involve the dimensions of the bodies and which agrees with the formulæ of King for fine wires and of Hill for thermometer bulbs.

DISCUSSION.

Mr. F. J. W. WHIPPLE said he presumed the author took both forced and free convection into account. There were many meteoric problems to which the application of the theory would be of value. Aitken had compared the radiation and convection losses of bodies by exposing them to the sun and measuring their rise in temperature. Using a series of blackened cubes, he had obtained values for the convection which agreed roughly with Barratt's square root law, and would no doubt also fit in with the results of this paper.

Mr. GOSLING pointed out that formula No. 13 appeared to make the convection loss increase with the

viscosity of the gas. Langmuir had arrived at the opposite conclusion.

Mr. J. GUILD asked if in applying the theory of dimensions to the heat loss from bodies of different sizes, the considerations were not vitiated by the fact that the size and mean free path of the gas molecules were not varying with the other parts of the apparatus.

The AUTHOR, in reply, said that the effect mentioned by Mr. Gosling was apparent only. Actually from the nature of the other terms involved, the equation gave reduced values of the convection loss as the viscosity increased. As regards the invariant size of the gas molecules, mean free path, &c., probably the equations cease to hold when any of the dimensions become comparable with the mean free path of the gas.

A paper entitled "The Radiation from a Perfectly Diffusing Circular Disc," by J. W. T. WALSH, was taken as read, the author being absent.

NOTICES OF BOOKS.

Intermediate Text book of Chemistry. By ALEXANDER SMITH. Pp. vi+520. 1920. London: G. Bell and Sons, York House, Portugal Street, W.C. 2. Price 8s. 6d. net.

THE author has named this book "Intermediate," because it is shorter than his College Chemistry, but longer than his Elementary Chemistry.

The book is divided into forty-three chapters, these giving divisions in the book. Chapters on Agricultural Chemistry, Foods and their Heating Values, and the Softening of Water are contained therein.

The chapter on Agricultural Chemistry contains articles on Plants, Fuels, and Food. It contains a brief outline of the substances used by plants as food and of the conditions which favour the growth of plants.

Chapters XXXI. and XLIII. deal with the recognition of substances, Chapter XXXI. with the non-metallic elements, and Chapter XLIII. with the metallic elements.

Organic Chemistry is introduced into the book only so far as to give a clear idea of the subject under discussion; for instance, in Chapter XXXII., on Fats, Soaps, and Related Compounds, and in Chapter XXXIII. on Explosives and Plastics.

Physical Chemistry enters into the book a great deal, several chapters being devoted to the discussion of its different branches.

In an appendix are given several useful tables, such as (1) the solubilities of bases and salts in water at 18°, (2) vapour pressure of water, (3) order of activity of the metals, and (4) International Atomic Weights (1917).

The book appears to be remarkably free from errors, and should prove a valuable help to those intending to take higher examinations in Chemistry.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxx., No. 21, May 25, 1920.

THE PLATING OF ALUMINIUM AND ITS ALLOYS.—MM. Léon Guillet and Maxime Gasnier.—The plating of aluminium and its alloys has been considered, till very recently, as an operation giving very unsatisfactory results owing to the feeble adherence of the deposit. A method, shown by M. Tassilly (*Revue de Métallurgie*, 1914, Mémoires, p. 670), based upon the previous attack of the metal by hydrochloric acid, has given commercial results. Having come to the conclusion that the adherence of the

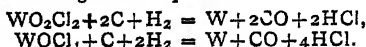
deposit was simply due to an imperfect surface on the metal, the authors tried the very simple mechanical means and very effective method of producing this imperfection, that of spraying the surface with sand. The first results were very favourable, and the authors found that the following points had to be remembered in order to obtain the best results:—

- The quickness with which the grains of sand were projected on to the surface of the metal, which depends on the pressure of air employed.
- The size of the grains.
- The time elapsing between this operation and the plating.
- The thickness of the covering of nickel.

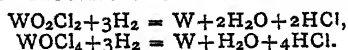
The authors then give the results of their researches together with their conclusions:—The "sand blasting" should be carried out at a pressure below 1500 grms. per sq. cm., with sand passing through a sieve of 2/10 mm. mesh. For a thickness of the deposit of 6/1000 of 1 mm.—time of operation, a half-an-hour, with a current below 0.8 ampère per sq. decimetre.

Chimie et Industrie, April, 1920.

TUNGSTEN.—M. Camille Matignon.—In the April issue of this journal M. Camille Matignon gives the second half of his paper on tungsten, which includes the manufacture of tungsten wire for electric lamps. The author has divided the processes of manufacture into three classes:—(1) Substitution, (2) by the help of an organic paste, and (3) by the use of colloidal tungstic acid. With regard to the first class, a carbon filament is brought to incandescence by an electric current in an atmosphere of hydrogen and tungsten oxychloride, thus giving a metallic filament according to the equations—



The disappearance of the carbon is manifested by a distinct improvement in the conductivity. At this stage the temperature is raised and the proportion of hydrogen is increased. The reduction continues as follows:—

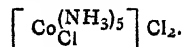


Tungsten wire is also made by mixing tungsten powder with an organic paste, such as sugar, gum-arabic, dextrin, &c., and drawn into a wire. These wires are calcined in a reducing atmosphere, after which the wire is a mixture of tungsten and carbon. The wire is a sufficiently good conductor to allow an electric current to pass through it, so as to raise the temperature to 1100°, which is carried out in an atmosphere of hydrogen containing a little water vapour. The water vapour oxidises the carbon, but the metal is protected from oxidation by a sufficient pressure of hydrogen. During this operation the wires shrink to about three-fourths of their length, at the same time assuming a metallic lustre. The third class is the employment of colloidal tungstic acid, which has the advantage of not having to get rid of carbon. Wires obtained by one of these methods have a good metallic lustre, but they are brittle when cold. When warm they are pliable. The life of tungsten wire lamps is limited because of the tendency of the wire to become crystalline.

Revue des Produits Chimiques, May 15, 1920.

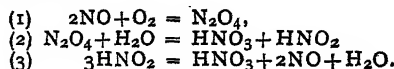
PHYSICO-CHEMICAL RESEARCHES INTO THE CONSTITUTION OF THE COBALTI-AMINES.—M. A. Job.—The researches of M. A. Job on the cobaltic pentamines have led him to adopt the general formula $\text{Co}(\text{NH}_3)_5\text{X}_{3.4}\text{Ag}$. X stands for an electro-negative monovalent radical (e.g., $\frac{1}{2}\text{SO}_4, \text{Cl}, \text{OH}, \text{H}_2\text{O}, \text{NO}_2$, &c.). This gives the series Roseo and Purpureo. In the Purpureo series one of the X-

radicals is taken into the electro-positive radical. For example, if the chloride is treated with silver nitrate only two atoms of chlorine are precipitated, according to the formula—



No. 10, May 31, 1920.

SYNTHETIC NITRIC ACID.—M. Paul Pascal.—The author gives a *résumé* of the methods employed now and in the past of making nitric acid from its elements. He divides his treatise into two parts; those methods based on the oxidation of nitrogen, and secondly by combining nitrogen and hydrogen to form ammonia and the combustion of this latter product. The basis of producing the oxidation of nitrogen is by combining oxygen and nitrogen by means of an electric spark as shown first by Cavendish. The author mentions several types of furnaces used in the operation. The oxidation and hydrolysis are expressed by the following equations, with nitrous acid as an intermediate product:—



Reaction (1) requires a high temperature, Reactions (2) and (3) are very rapid; they are opposed by a rise in temperature and by the presence of nitric acid in the watery liquor. The nitric acid liquor is concentrated either by concentration in vacuum or by distillation with sulphuric acid. With respect to the combustion of ammonia, catalysis comes into play, and MM. Pascal and Decarrière have studied various forms of catalysers (*Bull. Soc. Chim.*, Sept. 19). They found that the mixture only reacted with an appreciable speed above a certain temperature, which depended on the form in which the platinum was used, but not on the duration of the contact. The oxidation of ammonia by air in the presence of platinum gives, first, nitric oxide and water; the nitric oxide is transformed by contact with the oxygen in the air into N_2O_3 , NO_2 , and N_2O_4 (which is only stable above 150°). The transformation of the dioxide into the peroxide is not instantaneous. In conclusion, the author says that to solve part of the problem of synthetic nitric acid it is necessary to unify more completely the methods employed and to increase their number.

NOTES.

M. KAMERLINGH ONNES has been elected correspondent of the *Comptes Rendus* for the Physical Section, in succession to Sir William Crookes.

THE REPORT ON THE ECONOMIC CONDITIONS OF GERMANY.—This Report treats of the dominant factors in Germany economic and industrial and shows the condition of paralysis to which that country has been reduced by the losses and liabilities of the war. The industrial machine is intact, but the wheels are turning very slowly. Even when the necessary raw materials are obtainable within the country the shortage of fuel and the reluctance of labour to exert itself reduce production to a fraction of what it was before the war. The collapse of credit makes very difficult and costly the purchase from outside Germany of materials for industries dependent upon foreign supplies. The report sums up the situation as follows:—"Germany has very nearly ceased to be a purchaser owing to the state of her exchanges, and we are presented with the spectacle of this country in urgent need of food and raw material lying impotent, unable either to satisfy her own requirements or to relieve her neighbours of accumulations which are rapidly becoming a burden to them. As Germany cannot buy, so also she cannot produce; she is, therefore,

as long as present conditions last, not a serious rival, neither is she able to pay what she owes as reparation.

THE TREND OF TRADE.—In these days of preoccupation with many things—the procession of wages claims, the sporadic strikes and rumours of strikes, the threat of capital levies, the difficulties of production, the scarcity of money, and the prospect, both welcome and unwelcome, of a break in prices—it is useful to watch the Board of Trade returns. They are an index, though not, perhaps, a complete one, to the main course of events. And for the last few months they have been consistently encouraging. Those for the month of May show an adverse trade balance of 35½ millions, which is the lowest figure for any month since the Armistice. Exports reached the record figure of 119½ millions, an increase of 85.4 per cent over the corresponding month of 1919, and of 12.3 per cent over the April, 1920, figure. The imports were 116½ millions, showing a percentage increase of 22.6 over the 1919 figure. Re-exports totalled 20½ millions, an increase of 76.2 per cent. To some extent, of course, these increases are due to higher prices, but the main thing is the fall in the adverse balance of trade from 40½ millions in April last and 59½ millions in May, 1919. Comparing the past month with May, 1919, the exports of iron and steel rose from £5,384,215 to £11,958,241, and of machinery and mill work from £2,502,610 to £4,851,193. Electrical plant, chemicals, oils and fats, and, indeed, all other manufactures, share in the increased activity. The advance indicated by these figures is encouraging, but it is still more valuable as an index to the rapidity with which the country would reach a really sound industrial condition if all ranks were united in augmenting production, and if the problem of national expenditure were tackled in a more drastic manner than seems to be within the power or the will of the present Government.

REVISION OF THE SERIES IN THE SPECTRUM OF BARIUM.—F. A. Saunders (*Astrophysical Journal*, January, 1920).—The spectrum of barium contains three systems of series, the triplets, the single lines, and the pairs. After making a careful study of all available data, including recent unpublished observations by King, the author has revised and extended the previously recognised series of triplets and single lines and has identified the lines corresponding to one or more terms of each of several other series. Altogether about 135 lines are assigned to one or other of sixteen series, which include four series of triplets, two triplet combination series; four series of single lines from single-line combination series, and two inter-system combination series. Accurate constants for these series are given. The fundamental and diffuse series of triplets are unusually complex, and these and other series show curious irregularities both in the relative intensities of the terms and in the wave-lengths. No simple formula of the ordinary type will give the frequencies accurately. The paper includes a brief explanation of the notation used in designating the different series.

GEOLOGY OF ANGLESEY.—The Minister of Agriculture and Fisheries desires to draw attention to the publication, by the Director of the Geological Survey of England and Wales, of a Memoir on the Geology of Anglesey; containing 980 xl pp., and illustrated by 347 figures, 61 photographic plates, and 17 folding plates (4 being coloured). Two volumes, cloth 8vo. By Edward Greenly. Price £3 3s. net. The description of the crystalline schists, and of the various gneissic, volcanic, and sedimentary rocks which are included in the complex, occupies Parts I. and II. of the book. The structures of these rocks are discussed, and the stratigraphical order in which they may have originally been formed is suggested. Part III. deals with Cambrian, Ordovician, Silurian rocks, the Old Red Sandstone, and the Carboniferous group in which are included the Coal Measures. The various igneous rocks intruded into them during Palaeozoic and Tertiary times are described, and a full discussion given of the fossils of

each formation. The history of the glaciation of the island and accounts of the more recent deposits are given in detail, and the development of the land surface is studied. Part IV. deals with the mining and various other industries, water supply, and agriculture. In connection with the memoir a new and revised Geological map of the county is published simultaneously. It is on the scale of one inch to a mile and is printed in colours to show both "Solid" and "Drift" deposits; price 2s. 6d. Copies of both map and memoir may be obtained through any bookseller from the Director-General, Ordnance Survey Office, Southampton.

ARE PROFITS NECESSARY?—The very mention of profits in some quarters nowadays is as efficacious, metaphorically speaking, of producing a human tornado equally as the waving a red flag in front of a bull is likely to be productive of remarkable evolutions on the part of that animal. The other spheres, where profiteering perhaps is the sole element of consideration, the question of what constitutes profit creates perplexing thoughts, and again, in higher circles, the manifold problems associated with profits and profit-making are exercising the minds of our most advanced thinkers. In point of fact, it is a topic of debate in all countries, a topic which all seem to realise the importance of, yet opinions on many issues involved seem as divergent and wide apart as are the poles. It makes one wonder whether a point on which commonality of interests can mature will ever evolve. In this month's issue of the *Industrial League and Council Journal* is an article on "Are Profits Necessary?" contributed by Mr. E. J. P. Benn, C.B.E., in which the writer illustrates clear lines of demarcation. "It makes my blood boil," he says, "when I see some Polish Jew land on these shores and, within the space of a dozen or twenty years, become a millionaire. There is something wrong with a system which will keep a highly educated man of science working all his life in comparative poverty and allow an illiterate, vulgar, fat cosmopolitan financier to amass wealth to his heart's content. The capitalistic system, the profits system, will not, in my judgment, stand examination from the ethical or Utopian point of view. Morals should exercise an influence over industry, as, indeed, they should influence all our actions. But to substitute morals for actions themselves does not, unfortunately, work out as we should like it to. It does not give us houses; it does not reduce prices; it does not increase supplies and it does not add to our material comfort. Industry, to me, is something which is concerned with the feeding and clothing and housing of my wife and children; moral is, on the other hand, something which enables me and them to lead a better life. The two things are inextricably mixed up together, but they are not, and never will be, substitutes one for the other. Taxation of all kinds does not, as is commonly supposed, reduce the rate of profits; it merely turns the profit-maker into a tax-collector, and he, very naturally, charges another profit for collecting the taxes. But the commonest fallacy is that you can reduce profits by increasing wages, or that wages come out of profits, or profits out of wages. Nothing of the kind is, in fact, true. I therefore come to the conclusion that, in the present state of development of the human race, there is no more chance for platonic industry than there is for platonic love, and I do not want to see civilisation destroyed and the human race reduced to savagery and starvation by the chasing of an ideal which may apply to angels, but cannot apply to mere mortals. If instead of endeavouring to exterminate the profiteer we were to encourage him, there would be so much competition among profit makers as to reduce profits to an economic level. That is the business-like thing to do." Many other interesting articles, including those on the subject of "Profit Sharing" and "Economic Production and Prevention of Waste," are contained in the *Industrial League and Council Journal*, copies of which can be obtained from any station bookstall.

NOTICES.

EDITORIAL.—All Literary communications, and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

SUBSCRIPTIONS. £1 12s. per annum, payable in advance, should be addressed to the MANAGER.

BACK NUMBERS and VOLUMES can be purchased on application to the MANAGER.

ACC UNITS for Advertisements up to March 31 should be paid to the MANAGER.

THE CHEMICAL NEWS,
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ADVERTISEMENTS.

All communications for this Department should be addressed to—

T. G. SCOTT & SON,
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Assistant Chemists for shift work, and a Senior Assistant wanted in Iron and Steel Works Laboratory. State age, experience, and salary required.—Address, The Secretary, Consett Iron Co., Consett, county Durham.

ASSISTANT CHEMISTS wanted at once for the Admiralty Inspection Laboratories at Holton Heath. Candidates must have a qualification equivalent to that of the Association of the Institute of Chemistry, and must possess a sound knowledge of Technical Analysis, preferably explosives.

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Applications, stating qualifications and experience, should be made by letter to the INSPECTOR OF NAVAL ORDNANCE, Holton Heath, near Wareham, Dorset.

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The Governors of the above Institute invite applications for the Post of ASSISTANT CHEMICAL LECTURER. Must have good Honours Degree. Commencing salary £750 per annum. Particulars and forms of application to be obtained from the Clerk to the Governors.

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Applications are invited for the HEADSHIP OF THE CHEMICAL DEPARTMENT, now vacant by the appointment of Dr. T. S. PRICE as Director of Research to the British Photographic Research Association.

Full particulars of the appointment can be obtained from the SECRETARY, Municipal Technical School, Suffolk Street, Birmingham.

NOTICE.

OWING to the greatly increased cost of printing and paper, and the advance in the postal rates, we have been compelled to raise the price of the CHEMICAL NEWS from 4d. to 6d. (by post 7d.). The new subscription rates are as follows:—

Yearly (52 Nos.)	-	-	-	£1 12 0
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NOTICE OF REMOVAL.

On Friday, July 9, 1920, the Publishing and Editorial Offices at 16, Newcastle Street will be closed for the purpose of removing to

97, SHOE LANE, LONDON, E.C. 4,
which will be opened for business at 10 a.m. on Monday, July 12.

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Applications should be forwarded, not later than JULY 15 next, to the REGISTRAR, from whom detailed conditions may be obtained.

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3143.

EDITORIAL.

WITH a view to increasing the usefulness of the CHEMICAL NEWS, it has been decided to introduce in the near future a new feature in the method of publication. It was the aim of the late Sir William Crookes, that the CHEMICAL NEWS should be the medium for the publication of original thought among Chemists and Physicists, and in its columns most of the discoveries of the past fifty years have appeared; in some cases the CHEMICAL NEWS was the first organ of publication.

The present Editor desires that the Journal shall maintain its useful character, and is anxious to meet as far as possible the many suggestions that have been made to this end.

Recently numerous original communications have been received, but lack of space and difficulties in printing have caused delay in publication; these difficulties are likely to increase rather than diminish.

It has therefore been decided to arrange a weekly "Editorial Notice", to announce, and if possible give a brief summary of, any papers received during the week, but of which, for the reasons stated, publication may have to be deferred.

The Editor therefore suggests to authors that a short summary should accompany original communications, so that an announcement can appear immediately. Such announcements must be very brief, and should at most occupy but a few lines, giving only such details as are necessary for immediate publication.

The Editor would be grateful for any further suggestions that would help to make the CHEMICAL NEWS of greater value to the profession generally and to maintain its character as a means of publication of original thought in Chemistry and Physics.

SUBSTANCES DISSOLVED IN RAIN AND SNOW.

DURING the period from 1908 to 1917, F. T. Schutt and R. L. Dorrance, of Ottawa, Canada, conducted a series of analyses of rains and snows that fell in that section of the country. In 1914, under the direction of Dr. N. Knight, of Cornell College, a similar set of investigations was begun with the rains and snows that fell at the town of Mt. Vernon, Iowa.

Mt. Vernon is a town of about 2,500 population and has no manufacturing of any kind, the nearest industrial centre being some 17 miles away. With this in view, the rains should be remarkably free from contamination from city smoke and gases.

The samples of water were gathered in two porcelain pans near the centre of the town, and every precaution was taken to prevent contamination of any sort before analyses were made. The rains were analysed as soon as possible after precipitation.

This work is a continuation of that done by J. E. Trieschmann, published in CHEMICAL NEWS, Aug. 1st, 1919.

During the year from October 9, 1919, to May 22nd, 1920, there was a total rainfall of 11.37 inches and a total snowfall equivalent to 2.07 inches of rain. During this period there were 21 precipitations of rain and 8 of snow. The total rain and snow as rain was 13.44 inches. The largest rainfall occurred on October 9-10th, when there fell 2.6 inches.

The appearance of sulphates in rain is ascribed to the sulphur in the smoke of the atmosphere. Mt. Vernon being only 17 miles from a manufacturing city, it is very probable that the presence of sulphates is due to smoke from this neighbouring city. During this period, the sum of 51.0306 pounds of sulphate as SO_2 fell per acre. The largest amount at any one time fell on March 4, which amounted to 34 parts per million of water, or 7.7137 pounds per acre.

A total amount of chlorine equal to 48.1644 pounds per acre fell during this time. This is equivalent to 79.36 pounds of sodium chloride. The presence of chlorine in rain is said by Dr. N. Knight to be due to minute particles of NaCl carried by air currents from the Atlantic Ocean. The largest concentration of chlorine appeared on December 2, when a light snow equivalent to 0.08 inches of rain fell. At this time, chlorine to the amount of 17.7 parts per million, or 4.0157 pounds per acre, fell. Notice is made of the fact that during the showers and periods of small rainfall, the greatest concentration of chlorine occurred. No particular reason can be given for this occurrence.

Nitrogen was determined in four forms: As nitrates (NO_3), as nitrites (NO_2), as free ammonia, and as albuminoid ammonia. Nitrogen in the forms of nitrites and nitrates is probably caused by its oxidation during electric discharges in the atmosphere.

A total amount of 0.62841 pounds of nitrogen as nitrate fell, the greatest amount, 0.3 parts per million, or 0.06806 pounds per acre, occurring on December 2 and on January 23, at which times snow equivalent to 0.08 inches and 0.50 inches fell respectively.

As nitrite there was a total amount of 0.03725 pounds per acre nitrogen, the greatest amount coming on March 19, equal to 0.02 parts per million of water, or 0.00453 pounds per acre. At this time 0.4 inches of rain fell.

The presence of ammonia is in all probability due to the action of soil bacteria in the process of the fixation of nitrogen.

Free ammonia equivalent to 2.8642 pounds of nitrogen fell in this period. The amount is very large in comparison with nitrogen as nitrate or nitrite. On March 4, nitrogen as ammonia equal to 2.30 parts per million, or 0.52181 pounds per acre, fell with 0.4 inches rain.

Albuminoid ammonia was less frequent in its occurrence, for 32 per cent of the rainfalls gave no tests for it. A total of 0.4974 pounds of nitro-

gen as ammonia in the albuminoid form fell, the greatest single amount coming on February 12, when 1.12 parts nitrogen per million, or 0.2541 pounds per acre, fell with snow, equal to 0.25 inches of rain.

The total amount of nitrogen as free and albuminoid ammonias was 3.3616 pounds per acre. The total amount of nitrogen as nitrates, nitrites, and ammonias was 4.02726 pounds per acre. Of the total nitrogen, 82.5 per cent was in the form of ammonias. More nitrogen occurred in free ammonia than in any of the other nitrogen compounds.

This work was carried on under the supervision of Dr. Knight, and grateful acknowledgment is made of his advice in connection with it.

Cornell College, Mount Vernon, Iowa,
June 18, 1920.

THE COMMERCIAL APPLICATION OF ELECTRICAL OSMOSIS.*

By JOHN SOMERVILLE HIGHFIELD, M.Inst.C.E., M.I.E.E.;
W. R. ORMANDY, D.Sc.; and D. NORTHALL-LAURIE, F.I.C.

THE study of matter in the colloidal state is one of the first importance and is of surpassing interest. The problems resolve themselves into the scheming of methods of studying the rate of movement and the causes of movement of particles of very small size often approaching molecular dimensions. The forces causing movement are molecular, chemical, and electrical, added to the force of gravitation, and the movements may take place in any medium, but usually in water. The importance of the subject is apparent when it is realised that many of the largest trades and manufactures depend on the use and proper treatment of matter in the colloidal state. Agriculture depends on a suitable colloidal state of the soil, tanning of leather on the introduction into the cells of matter in colloidal form. The glue and gelatin industry deals with colloidal matter. The dyeing of fabrics consists largely in introducing finely divided material into fibrous matter. Again, by a scientific study of their slimes the efficiency of the recovery of metals can be increased. Paper-makers deal with matter in a colloidal state. Trades so diverse as dairy production and paint manufacture are equally concerned in the treatment of colloidal matter.

The terms colloid or matter in a colloidal state, true solution and suspension, are not easy of simple definition. For the purpose of the immediate subject, matter in a colloidal state or a colloid means matter in so fine a state of division that it tends, under favourable circumstances, where coalescence does not readily take place, to remain for some hours in suspension.

The term Osmosis, or Osmose, appears to have been first used by Graham about 1854; it may have been derived from the Greek word *Osmos*, meaning "pushing," and the terms *Exosmosis* and *Endosmosis*, used by Dutrochet about 1800, refer to a pushing outwards or inwards, osmosis being a general pushing such as the diffusion of liquids through a diaphragm. The importance of the phenomenon has long been recognised, as it is

one consistently occurring in living bodies, both animal and vegetable. The first record appears to be by Nollet (1700-1770) as a result of experiments with water and alcohol through a bladder. Dutrochet investigated the subject, and his work resulted in numerous applications in methods of dialysis by Graham. Graham insisted that the phenomenon was molecular, and that it is due to the raising of sap in trees against gravity.

Graham, in 1861, found that when a weak solution of sodium silicate was poured into excess of hydrochloric acid no precipitate was formed, whereas, if the sodium silicate solution was strong, a gelatinous precipitate of silica was obtained.

He found that by placing this clear solution in a small dish made of parchment, and floating it in water, the sodium chloride produced by the reaction passed through the pores of the parchment paper, and, by frequent changes of the surrounding water, could be completely removed, leaving inside the dish the silicic acid, thus proving that it was not an ordinary solution.

Graham called the silicic acid when in this condition a *Colloid*, whereas he termed the salts and other similar bodies that passed through parchment *Crystalloids*, and the separation of one from another *Dialysis*.

These original definitions have been extended and amplified. A colloidal solution is termed a *Sol*, and, if water is the liquid in which it is contained, the sol is known as a *Hydrosol*; if alcohol, an *Alcosol*, or generally an *Organsol*, if the medium is some organic liquid.

The colloidal substance is termed the *Disperse Phase*, whereas the medium in which it is dispersed is termed the *Disperse Medium*. Most materials, including metals, sulphides, oxides and salts can exist in the colloidal state. Natural substances occurring in very small particles such as ball-clay, china-clay, and the various types of fire-clay, can be brought into the colloidal condition by suitable means, and most naturally occurring compounds, as emery, quartz, or steatite, and the artificial abrasives, carborundum and alundum, can be rendered colloidal by sufficiently fine grinding.

The existence of a material present in the colloidal state in a so-called solution can be demonstrated in various ways. For instance, when the colloidal particles are extremely minute their presence as particles can be shown either by dropping upon filter paper, when the colloidal matter will remain as a stain in the centre, the disperse medium, in this case water, spreading out around it; or by passing a powerful beam of light through the liquid, when the particles will cause the path of the beam to become visible, and the light reflected from the particles to be polarised. This experiment was first shown by Tyndall, and is known as the Tyndall effect.

Electrical Properties of Colloidal Solutions.—Picton and Linden found that matter in colloidal suspension, when subjected to direct current of upwards of sixty volts between platinum electrodes, tended after a time to collect either around the anode or cathode, leaving a clear space around the cathode or anode respectively.

They investigated this phenomenon and found it to be of general occurrence. It is known as Electrical Osmose or Cataphoresis, and the

*A Paper read before the Royal Society of Arts, May 19, 1920.

polarity of the particles depends not only upon the constitution of the particles but on the nature and quantity of electrolytes present, and also upon the composition of the disperse medium in which they are suspended as the disperse phase. Thus, silicic acid is charged positively when in water, and negatively when in turpentine.

Generally, the continual suspension of a colloid in the disperse medium is possible only when the colloidal particle retains an electrical charge. The particles possessing the charges of the same sign, either positive or negative, repel each other, and so cannot coalesce or coagulate together.

They can be made to coalesce by subjecting them to an electric field by means of immersed electrodes, when they are attracted to the pole of sign opposite to their charge, and are so discharged; this is the industrial method used in the purification of clay.

They can be made to coalesce by adding to the liquid an equal number of colloidal particles of opposite charge, when the two sets of particles mutually discharge one another. As an example, the addition to a colloidal suspension of arsenic sulphide of a colloidal suspension of a basic material, such as ferric hydrate, causes the precipitation of the two colloids.

The quantity of one colloid required completely to precipitate another colloid of opposite charge varies with the composition of the precipitating colloid. Biltz gives the following figures: 1.4 m.g. of gold is completely precipitated by:—

- 4 mgrms. of cerium oxide;
- 3 mgrms. of ferric oxide;
- 2.5 mgrms. of thorium oxide;
- 1.6 mgrms. of zirconium oxide;
- 0.3 mgrms. of chromic oxide;
- 0.1 to 0.2 mgrms. of alumina.

The order of power of precipitation varies with the substance to be precipitated, and depends probably upon the absorption capacity of the material.

Another method of bringing about the coagulation of peptised particles is to add to the suspension of a small quantity of a salt which in solution is subject to electrolytic dissociation. If the peptised particles carry an electro-negative charge, then the added electrolyte must be electro-positive; thus, bodies which are peptised by an alkali are precipitated by an acid.

The deposition of the fine silt and mud carried down by rivers when the stream encounters the salt of the sea is, no doubt, due to the flocculation of the dispersed particles by the salt electrolyte.

In order that the phenomenon of electrical osmose can be shown, it is necessary first that the colloidal material in suspension should be broken up by giving each minute particle an electrical charge, thus preventing coalescence, that is to say the suspension should be peptised.

Various materials can be peptised, each requiring different peptising agents: thus, gelatin is peptised by hot and not by cold water; gums by cold water; mastics in alcohol by large quantities of water; metals by fused metallic salts; hydrous oxides by caustic alkali.

The special application of these principles, to which we wish particularly to refer, is the purification of clay and similar materials. The commercial application of these phenomena to the purification of the clay is due to the late Count

Schwerin. He showed that the addition of small traces of alkali to a suspension of clay in water resulted in the suspension becoming highly mobile, the clay particles remaining for a long time in suspension, the pyrites, mica, free silica, and other impurities which are not peptised, tending to fall through the suspension.

Count Schwerin, in his patent specification, points out that bodies in suspension which tend to move to the cathode, require an electrolyte of an acid character to be employed to bring about dispersion or peptisation, but that bodies which tend to move to the anode require electrolytes of an alkaline character. It is further of interest to note that the original inventor not only shows that the addition of suitable electrolytes can be used to peptise the main matter in suspension, to bring about increased fluidity with the object of allowing foreign matter to separate out by subsidence, but he also points out that if one substance is present in varying degrees of fineness, it is possible by the utilisation of the same principles to bring about a separation of the fine particles from the coarse ones.

Coalescence of the peptised particles in a clay slip can be produced by discharging the particles by the addition of acid to the suspension; the clay then settles in a gummy flocculated mass, carrying with it the fine impurities as previously explained. The action of the acid and alkali on the slip can be illustrated by reversing the method and allowing a thin stream of neutral clay slip to flow into a vessel containing on the one hand acid, and on the other alkali; in the first, the clay particles fall in a continuous solid stream and settle quickly; in the second, the clay particles spread out broadly and settle very slowly.

There are many disadvantages to the flocculation of the clay by coagulating with electrolytes; certain fine impurities remain in suspension and are carried down with the flocculated clay, so that only partial purification is attained. The physical state of the clay is entirely altered, and the clay is left in a form difficult to collect and dry. For these reasons, the electrical method of purification was developed.

If, in the prepared suspension, two electrodes are immersed, and a difference of electrical potential be established between them, the clay particles move to the anode, where they discharge themselves and adhere as a coagulated mass, and the water is driven to the cathode, leaving the clay in a semi-dry state attached to the anode. The fine particles of silica, mica, pyrites, and other impurities, either migrate to the cathode or are washed away by the water stream moving to the cathode.

This is an example of using direct electrical pressure to produce coalescence in a peptised suspension.

The effect of the practical application of the process on clay is to remove particles of mica, silica, pyrites, and felspar, and to leave the clay substance in a satisfactory state for final drying. (The effectiveness of the purification was illustrated by reference to photo-micrographs).

It is, perhaps, allowable at this stage to indicate some of the directions in which the osmotic treatment of clay leads to advantages, having a direct and practical bearing upon industry. It is not realised sufficiently that the melting-point of pure

clay substance is higher than that of any admixture of common clay substance with silica, although it is commonly known that the other ingredients generally present in mined clay, such as pyrites, mica, feldspar, and the like, are very active in reducing the melting point. The more finely divided the silica and other impurities, the more intense the action in bringing about the softening of the clay substance at high temperatures, for the fine state of division brings about a great area of active contact surface. It is this fine material that cannot be removed by settling, and which the Osmosis process successfully eliminates.

The sintering or vitrifying temperature of a clay may be taken to be the temperature at which the rapid contraction of the clay in firing ceases; above this point little contraction occurs. Sintering takes place in osmosed clays at lower temperatures than in raw clays; consequently, goods made with osmosed clay can be finished at lower temperatures, resulting in a saving of fuel. The reduction of the sintering temperature, together with the higher melting-point, enables articles to be made that show little further contraction after burning. The amount of the reduction of the sintering temperature varies for different clays; it is as much as 300° C. for low-grade clays, and much less for high-grade clays. Bricks made from some clays, after osmosing, are better burnt at 1100° C. than from the raw clay at 1300° C.

Many alluvial red-burning clays cannot be fired to vitrification because, before vitrification temperature is reached, the clay commences to blow. Many such clays, after the osmosis treatment, have a margin of from 100° to 200° C. between the vitrifying temperature and the temperature at which decomposition starts. This enables vitrified bricks and vitrified roofing tiles to be made from a product which, without treatment, could not be used for such purpose.

In the manufacture of porcelain and earthenware, osmosed clays yield whiter bodies or bodies freer from specks and stains. Osmosed fireclays are entirely free from pyrites, and goods made therefrom are not subject to green stains when glazed.

By the use of fine osmosed materials, chemical porcelain has been produced of the highest quality, the body being made of pure kaolin only, which, owing to the fineness of the particles, completely vitrifies; the locking of the glaze to the body by the fine sillimanite crystals, which form on firing and penetrate the glaze, was shown in a photo-micrograph.

The form given to the apparatus for the commercial purification of clay consists of a tank of suitable form, containing at the lower part two paddles, which serve to keep the suspension in agitation, and which direct it in a stream through the numerous small spaces in the cathode fixed immediately above, surrounding the lower half of the anode. The anode consists of a metal cylinder, revolving at a speed of about one revolution in three minutes, at a distance of about three-quarters of an inch from the cathode. A scraper removes the clay from the anode, whence it falls down a chute clear of the machine. The fresh clay suspension is fed into the lower part of the container, and the water effluent returned to be mixed with fresh clay. A machine with a cylinder, two feet diameter and five feet long,

produces about 1000 tons of pure clay per annum.

The manner in which the machine acts towards the clay slip is as follows:—

The clay in suspension, in passing through the laminated or perforated cathode, becomes negatively charged and is immediately attracted to the anode cylinder, the water being driven towards the cathode. There is thus obtained a dry layer of clay on the anode cylinder and a watery zone of clay suspension round the cathode. Fresh clay entering the machine encounters the watery zone on its passage to the anode, in which zone the electro-osmotically indifferent particles such as pyrites, mica, and quartz, become freed from the clay, and are washed away with the effluent from the machine. The effluent with these particles also contains some clay. It is carried to a settling tank where the impurities quickly settle out, and thence to a blunger, or other mixing machine, where it takes up fresh clay and returns again to the machine through one or more settling tanks.

The clay leaves the machine in the form of a blanket from one-quarter to one-half of an inch in thickness, from which all the water has been driven except about 25 per cent, and in this form admits of ready drying when required. The process is extraordinarily flexible and, therefore, lends itself to the treatment of many varieties of clay from which many different products are obtained. From some marls and fireclays, considerable quantities of pyrites are obtained, and from others silica in a very finely divided form is separated. From china-clay deposits, exceedingly fine mica and sand are obtained. Again, the clay particles themselves vary greatly in fineness, and the very fine particles can be separated from the coarser. This exceedingly fine clay is useful for many purposes, and doubtless many new applications of its use will arise. The finest particles of ball clay are almost jelly-like in fineness.

The cost of working varies widely according to the class of clay treated. The electricity used varies from as low as 20 up to 70 units per ton of machine product.

Another application of electro-osmosis is the electro-osmotic filter press, which has been developed for the de-watering and purifying of many substances in a finely divided state. The press in its simplest form consists of a series of chambers into which the suspension is fed under a head of, say, 10 ft., sufficient to ensure a rapid filling of the chambers. The chambers are closed on both sides by filter cloths in the ordinary way, but the cloths are held in position by perforated or grooved metal or carbon or other conducting plates, one of these plates forming a cathode and one an anode. An electrical pressure of 20 to 100 volts, depending on the substance to be filtered, is established between the plates, and the water is forced towards the cathode. In this press, very fine materials can be de-watered, materials fine enough to choke the ordinary press. This press can be used for filtering clays and many other materials in a colloidal state which are difficult to filter in the ordinary pressure press.

The application of the principles of electrical osmosis are by no means confined to the purification of clay. The applications are, in fact, so many that it is possible in the time at our disposal to refer only to a few examples, such as the tanning of leather, the treatment of metallic

slimes produced in various stages of metal purification. The removal of ash from gelatin and the separation of glue and gelatin into several products has been accomplished.

(The paper was illustrated by a large number of lantern slides and experiments.)

DISCUSSION.

The CHAIRMAN (Mr. A. A. Campbell Swinton), in introducing Mr. Highfield, who read the paper, said the subject of electrical osmosis was one that was partly chemical, partly electrical, and partly physical, and in its applications came into the region of engineering, so that it was perhaps reasonable that three authors should have taken part in the paper—Mr. Highfield, who was a member of the Council of the Society and well known in the electrical world, Dr. Ormandy, who was well known in the electrical world, and had previously lectured before the Society, and Mr. Northall-Laurie, who was also a distinguished chemist.

Sir HERBERT JACKSON, K.B.E., F.R.S., said he had been always interested in electrical osmosis, and at the time during the war when there was some anxiety as to the supply of glass, the hope of getting something better in the way of pots for optical glass was of importance, and it was realised that if the lines pointed out in the paper could be followed it would be of great benefit. The facts were very simple and clear with regard to the advantages of the clay. In his own case, in using an ordinary and well-known form of clay crucible or muffle for experiments, he was very lucky if he could ensure getting anything like 24 hours' work out of it, but it was quite easy to obtain something in the order of ten or fifteen times as much work out of a muffle that was produced from the osmosed clay. He exhibited two specimens of crucibles which had been given to him by the authors, one of which had been baked at a temperature between 800° and 1000°, and the other had been used as an experiment to see how far it would contract at a higher temperature, and inside it and fused into a mass that was quite soft, was some of the clay of a crucible that he at one time used, so that the ordinary clay crucible had fused inside the authors' crucible. When the crucible was being taken out of the furnace, which had a pure silica lining, it had to be lifted out with considerable force, and the silica was drawn out in fine rods, but it was not possible to deform the clay crucible even in taking it out with considerable force. When material was in a fine state of division, so that each particle could exercise its best attraction on the neighbouring particles, a condition of equilibrium and great stability was reached, and when there was stability under heat there was also stability under chemical action for most things. There was great hope that many things which had been difficult to prepare with ordinary clay could be prepared in a state of greater purity and more readily when the process of the osmosed clay was understood thoroughly and became regularly used. He had had the pleasure of meeting Dr. Ormandy and Mr. Highfield some time ago, and took the whole matter up with Dr. Ormandy, and they started out and achieved the brilliant success they had shown that evening, and he felt confident it would be as

brilliant a success when carried out on a large scale.

Mr. WALTER C. HANCOCK said those who had had any experience in the preparation of a lecture for such an audience would be very much impressed with the magnificent show the authors had given. The photographs, taken under very high magnification, were really quite triumphs of art. He did not think he would be giving away any secrets if he said that he came to the meeting that afternoon from a place where they had been more or less discussing the problem of the production of glass, and he was happy to say that the production of high-grade optical glass of all descriptions was now being wrested by this country from many former competitors, and success would depend entirely upon the utilisation of some high-grade refractory material. Up to the present, manufacturers had been content to take the raw material as it was mined and submit it to the most primitive methods of purification. The osmosis process would supersede any method employed hitherto for the production of high-grade china-clay and other forms of clay, and a material would be obtained which was capable of resisting the effects of high temperature on the one hand and of chemical action upon the other.

Mr. W. MURRAY MORRISON said he had seen a large number of samples of osmosed clay, and he believed there was a very large field of application for that clay in this country; in fact, it would seem that the field was almost unlimited. The Society was very much indebted to the authors for having brought the subject forward.

Mr. W. H. PATCHELL said the slides shown on the screen were very beautiful, but the specimens were more fascinating still when seen under the microscope. With regard to the question of colloids, he thought the first strike on record was due to colloid chemistry, when the Egyptians cut off the supply of straw from the Israelites for making bricks. In 1910 he saw the work on osmosis being carried out by Count Schwerin in Germany, and he sent some samples of clay from Cornwall and received most beautiful results from the Count, but he did not appreciate at that time what those samples really meant. They showed a finer clay than could be produced by the ordinary method adopted in Cornwall, but there was no demand in this country for such beautiful products; it was said not to be commercial and so was turned down. About three years later he had one or two interesting interviews with Dr. Ormandy, and after that Sir Herbert Jackson took the matter up. The Cornishman, though generally a Radical, was a most conservative man in his methods. The ordinary Cornish clay washing had gone on with practically no change whatever, and when the offer was made to show the Cornishman better methods it was very difficult to get him to move, and as he could sell more clay than he had been able to produce he really could not be blamed. The difficulty now was not in producing the clay but in getting it out of Cornwall. Where very pure products were required the new process must be of very great benefit.

Captain C. J. GOODWIN said he noticed in a paper by Dr. Ormandy he referred very extensively to the use made of the osmosis process in Germany. It was no secret that Dr. Ormandy and probably some of his colleagues had again visited

the Continent, and it would be of great interest to know to what extent the process had been used during and since the war in Germany and other foreign countries. Apparently the industry was in its infancy in this country. He was anxious to know whether anything had been done to apply the process to the drying of peat. It was a very important question at the present time, because of the great shortage of fuel. In some Continental countries, notably Italy, lignite and peat deposits could be very well utilised if they were amenable to that sort of treatment. In the chemical industry of nearly every country there were certain by-products and factory wastes which were to some extent of the colloidal nature, and those products very often contained material which, if it could be sufficiently recovered, would yield a very handsome profit. One of the commonest instances was perhaps sewage, in connection with which considerable use had been made of centrifugal machines and filters. It would be interesting to know how the osmosis process would compare with other methods that were used, and to have some idea of what the cost of treating the clays was, in order to have a comparative basis in considering the problems. There was also the question of the conditions under which various bodies were capable of undergoing osmosis treatment. The authors had dealt almost entirely with suspensions in water, and he would like to know whether the process was at all applicable to materials suspended in other liquids, such as ferric hydrate in a caustic soda solution or arsenical suspensions in sulphuric acid. He noticed that the clay separated out very rapidly, and he would like to know what the weight of separation was, and whether it varied to any considerable extent with different materials. At the present time considerable interest was being taken in the question of suspension of coal dust and other combustible material in oil, to which the generic name of "colloidal fuel" had been given and it occurred to him that possibly investigation into the time required for the separation might be a useful method of determining the efficiency of those suspensions in oil.

Dr. W. R. ORMANDY, in replying to the discussion, said a very fine piece of work was involved in the coloured photographs which necessitated Mr. Northall-Laurie working very late hours, as even the vibration of passing traffic would ruin the photographs altogether. With reference to the remarks of Sir Herbert Jackson, an osmosed clay muffle, made from a certain clay, lasted thirteen journeys, heated up to 1500° C., as shown by the pyrometer, whereas muffles made from the same clay used by the muffle maker without treatment would never last three journeys. Taking the finest English china-clay which had been treated with 97 tons of water in order to wash 3 tons of clay, it was still possible to separate from that clay 7 per cent by weight of a product which consisted almost entirely of silica and mica and large rouleaux of china clay, which were not broken up or dispersed by the alkali. Mr. Hancock had rather emphasised the point raised by Sir Herbert Jackson that in the manufacture of optical glass there was a great demand for higher grade refractories than were available previously. That was not only due to the mechanical properties of the clay, but for optical purposes it was essential

that the clay substance itself should not enter into the mixture in a pot to any appreciable extent. As most fireclays contained a good deal of iron, iron, which was a colouring matter, was introduced. Therefore, for the optical glass maker, it was essential that he should have a crucible which would stand the high temperature and would not be eaten away by the corrosive action of the products which were being melted. In the manufacture of ordinary commercial glass there was a very great opening for the use of clay treated by the osmosis process, because at the present moment the great glass industries of this country, which were being developed to a degree unknown before the war, were severely handicapped by the kind of clay they had to employ for their tank blocks and for making crucibles. There was no question that an osmosed clay, owing to its refractory properties, would resist the corrosive action of the fluid glass in the tank. In the past manufacturers on the Continent had made great progress in the manufacture of glass, and if this country was to gain the industry to supply not only our own requirements but the world's markets, it would be necessary to recognise that the methods that were used by the Egyptians were still largely in use to-day, and were methods that had to be scrapped. It was no use stating that science was a great thing unless the manufacturer was going to support science and apply it. With regard to Mr. Patchell's remarks, many people had the idea that the straw used in Egypt was mixed into the bricks in the form of a binder, but that was not the case. The Egyptians used to put the straw into tanks and allow it to ferment in a hot climate until it went into a colloidal rotting mass, and that was used to mix with the sandy Nile-clay in order to make it more plastic. The lack of demand in this country for purified osmosed china-clay in the early days merely showed that the users were not sufficiently educated to realise that it paid to use a scientifically purified product. The manufacturers had to be educated, and to a very large extent the directors of some of the big companies needed education. With regard to Captain Goodwin's remarks, the osmosis process was derived primarily from the Continent, where there had been a greater time to develop it. In Austria there were already china-clay works turning out 60 or 70 tons a day, and there were works at Klingerberg being worked by the process, and very large works with seven or eight machines near Coblenz, and plant was already being erected in Spain. With reference to the drying of peat, that was a subject that had occupied his and his colleague's attention very considerably. The osmose filter press was, in his opinion, the only method which had yet been offered that showed a possible outlet for the treatment on a commercial scale of colloidal peats, which could neither be centrifuged nor pressed. Unfortunately the bulk of peat in the world was of a colloidal type. Such peat could be treated by the osmosis process, and he thought no long time would elapse before Mr. Highfield would be in a position to deal with the matter in another paper. Sewage experiments had also been carried out. One of the troubles was that, whereas clay would travel from one pole definitely to the other, in sewage there was a heterogeneous mass of material, some of which went to one pole and

some to another, and some had no electrical property whatever and would not move. As far as his own experiments went, there did not appear to be any immediate prospect of the electrical treatment of sewage proving any solution of the difficulty. As to the conditions of use, it was quite obvious that a particle could not move in an electric field if there was a good deal of soluble salts present, and that ruled out the possibility of separating colloidal ferric hydrate from a caustic soda solution, as the soda would convey the current and a very large amount of electricity would have to be used. The only way in which colloids suspended in an electrolyte could be dealt with would be to use a modification of the process. First of all, the electrolytic salts should be removed from the solution, leaving the colloid in a watery solution, and afterwards it could be dealt with in the same way as clay. With regard to the rate of output, that was conditioned to a certain extent by the electric pressure used, but there was an economical rate which it did not pay to exceed. The figure for all clays seemed to be pretty much the same. The purer the clay the larger the output. Coal dust suspended in oil behaved as a pseudo-colloid and was subject to the same laws as clay suspended in water, but that was a branch of the subject which had only just come into prominence. It would have to come into very much greater prominence, because oil was getting in greater demand every day, and the supply was not growing at more than one-third of the rate of the demand, so that the question of mixing coal dust with oil was a problem of the very greatest importance.

Mr. HIGHFIELD said it was quite possible to dry peat economically; with a moderate consumption of electricity the water could be forced out of the peat, and when that was done the peat was in the form of little curled up bits of material like cocoanut shavings. The difficulty was to know what to do with the peat in that form. It could be made into a briquette, but that involved a further consumption of energy, and unless it was made into a briquette it was difficult to carry, because it was bulky, and the cost of freight was high. If a peat was mined on a really large scale, tens of thousands of tons a month, the difficulty would be that, as the peat lies in moderately shallow deposit, it would be always running further away from the plant, as the plant could not be placed upon the yielding beds, so that the cost of bringing the peat to the plant was continually increasing and there were many other difficulties to be overcome apart from drying. He had to thank his colleagues for the enormous amount of work they had done on the paper, and Dr. Ormandy for having answered the questions raised in the discussion. He also wished to thank his assistants, who had been of great help in preparing the experiments.

The CHAIRMAN, in proposing a hearty vote of thanks to the authors, was sure the audience would agree that the experiments had been beautifully shown, and that the whole demonstration had been a model of its kind.

The motion was carried and the meeting then terminated.

GRINDING WHEELS: THEIR MANUFACTURE, USES IN INDUSTRY, AND FACTORS AFFECTING THEIR SELECTION.*

By WALLACE T. MONTAGUE.

GRINDING is one of the most ancient of arts. Pre-historic man shaped his instruments of stone and later of metal by rubbing them on rocks which possessed abrasive qualities. It is not a matter of record when the idea of cutting out a circular block of stone, mounting it on a spindle, and revolving it by hand was first thought of.

Sandstones were originally used in the industries where grinding operations were performed, although the applicability of emery was generally recognised by the Greeks of the early ages, who found it on the island of Naxos. The extensive use of emery in competition with the sandstone was limited until around the year 1870, when a method was invented for binding the grains together with a suitable medium and forming the wheels into necessary shapes for use in grinding.

Improvements in the methods of manufacture of grinding wheels naturally included a betterment of the abrasive material, with the result that the artificial abrasive was developed to overcome the imperfections of the natural emery, and to make available an abrasive in sufficient quantity to meet the ever increasing needs of industry.

Abrasives.—In general, there are two types of abrasive—aluminous and silicon carbide, the former consisting essentially of aluminum oxide, and the latter of a chemical union of the elements carbon and silicon.

Aluminous abrasives occur in nature as minerals in the form of emery and corundum. Aluminous abrasives are also manufactured by electric furnace methods and sold under the trade names "alundum," "aloxite," "borolon," &c.

Silicon carbide abrasives do not occur in nature but are manufactured in the electric furnace and sold under such trade names as "crystolon," "carborundum," "carbolon."

The Norton brand of aluminous abrasive, alundum, is made from the natural mineral, bauxite, containing as high a percentage of aluminum oxide as it is possible to obtain. The ore is carefully analysed and a mixture so made that the product of the furnace operation is fully controlled. The mixture is fused in an electric furnace of the arc type, and during fusion the material is purified and changed from soft bauxite into hard crystals of aluminum oxide.

The Norton brand of silicon carbide abrasive, crystolon, is manufactured by heating pure silica sand and coke together in a special resistance type of electric furnace. The material is not fused, but a chemical reaction results from the high temperature employed, with resulting crystals of abrasive.

Sizing the Abrasive.—The alundum and crystolon abrasives are received at the Norton grinding wheel plant in irregular pieces about six inches in diameter. This material is passed through a series of jaw crushers, rolls, washers, &c., and is

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finally sized by being passed through standard mesh screens. The standard grain sizes begin at 8 mesh and continue through 200. The flour which is left is designated as 200-F, and is further refined and classified by hydraulic means into such sizes as F, 2F, 3F, XF, &c. The number giving the size of the grain indicates approximately the number of holes to the linear inch in the screen through which the grain will just pass. For instance, a 30 grain will just pass through a screen having 30 small holes to the linear inch or 900 small holes to the square inch.

After passing over the sizing screen, the abrasive grain is stored in tanks, ready to be sent out as polishing material or to be used in the manufacture of grinding wheels.

Manufacturing Processes.—Grinding wheels are manufactured by four processes—vitrified, silicate, elastic and rubber.

By far the larger proportion of grinding wheels is manufactured by the vitrified process. In this process, the abrasive grain is mixed with the proper amounts of clay and water until the mixture has the consistency of a mud, which can be easily poured into moulds. After pouring into moulds, the wheels are taken to drying rooms and left until they are thoroughly dry. They are then shaved on special shaving machines to the approximate shapes and dimensions required, and placed in dry storage, ready to go into the kilns for vitrification. Vitrification in the kilns takes place at about the melting point of steel, and the length of time required for heating, the length of time held at high heat, and the cooling period are very important. Kilns are of the type used in the pottery industry, and are fired by a series of hard-coal fires uniformly spaced around the base of the kilns. In the larger types of kilns, it is approximately three weeks from the time the kiln is charged, until it is drawn. This time is absolutely necessary, and regardless of the emergency nature of any order, every wheel burned in the large kilns must remain there for the full time. After the wheels have been burned, they are sent to machines where they are shaped to exact size by means of hard metal cutters.

Silicate wheels, as the name indicates, are made by using a bonding material composed of silicate of soda. These wheels are made by tamping into iron moulds, and they are baked at a comparatively low temperature. By this process, all wheels 30 or more inches in diameter are manufactured, 60 inches in diameter being the maximum size that can be made.

Elastic wheels are made by using a bond having quite a degree of elasticity. The bond is of an organic nature and is composed mostly of shellac. These wheels are also tamped into iron moulds and are baked at a comparatively low temperature.

Rubber wheels are made by mixing abrasive with rubber, and later, vulcanising the resultant product.

Silicate wheels are used largely in the cutlery industry in general to replace sandstone; and for all wheels over 30 inches in diameter, which cannot be manufactured commercially by the vitrified process. Elastic wheels are used where very thin wheels are required for cutting off stock; also for finish grinding of chilled iron rolls, and for other work where a fine finish is desired. Rubber wheels

are used on the same type of work as elastic wheels, except that they have a somewhat harder action and are, therefore, used only where grades harder than those made by the electric process are required.

Abrasive Action.—The abrasive action of an aluminous abrasive is dependent upon the amount of crystalline aluminous oxide present and also upon the temper or brittleness of the abrasive.

The best grade of emery comes from Turkey. It contains up to about 65 per cent of corundum, which is the form in which the cutting element occurs in emery. Emery mined in America has as low as 10 per cent corundum. The chief impurity of emery is magnetic iron oxide. Alundum abrasives contain more than 92 per cent of this cutting element, and a special alundum known as No. 38 contains more than 98 per cent aluminum oxide. Practically no magnetic iron oxide is present in these abrasives.

Artificial aluminous abrasives are more efficient than emery, because: (1) they contain a much higher percentage of cutting element; (2) being free from impurities, they are capable of variations in toughness to suit the work to be done; (3) they are made to a definite standard of composition and temper.

The grinding wheel to meet present day requirements must be a scientifically developed cutting tool. Its action when at work is similar to that of the steel milling-cutter. On the face of the wheel are millions of cutting teeth at work every minute, and although these teeth are not as long or as strong as the teeth of the steel cutter, and cannot cut as deep, they are capable of working at a much greater speed. Each little cutting tool, which in substance is a grain of abrasive material, cuts off a chip at each revolution. The chips resemble, in shape and character, the chips cut off by the milling-cutter.

Uses in Industry.—The uses of grinding wheels in industry to-day are many and varied. The great refinement attained in the case of the gasoline motor used for automobiles could not have been reached without the use of the grinding wheel and artificial abrasives. Likewise, the grinding wheel plays an important part in the manufacture of tractors, motor trucks, gas-engines used for farm purposes, &c.

The ball and roller-bearing industry, which has grown up alongside the automobile industry, is likewise absolutely dependent upon artificial abrasives for the refinement and accuracy of its product. Being composed of hardened alloy steels, the only way that these could be brought within the required limits of accuracy and finish is by means of such aluminous abrasives as alundum. Likewise, the requirements of this industry are so great that existing supplies of natural abrasives, even though they were of proper standards of purity, would not begin to meet the demand.

The phonograph, the typewriter, the adding machine, the cash register, and other apparatus of similar nature could not be made as economically to-day, if it were not for the grinding wheel industry and artificial abrasives. The agricultural implement industry uses grinding wheels and abrasive grain in large quantities for the manufacture of harvesting and threshing machinery, ploughs, planters, &c. Even such activities as the

textile industry require grinding wheels for sharpening cards, snagging castings, and maintaining tools, cutters, and dies used extensively in keeping up its equipment.

The leather and shoe industry uses grinding wheels for the buffing of hides and for the sharpening of leather cutting and shaving knives.

The steel-mills use alundum grinding wheels for grinding out seams of high-speed steel billets preparatory to rolling into bar stock. The steel foundries use alundum wheels for snagging steel castings. Crystolon grinding wheels are used in foundries for snagging cast-iron castings, and for cleaning castings of brass, bronze, and aluminium.

The railroad industry has extensive use for wheels composed of artificial abrasives. Such parts as locomotive piston-rods and valves must be ground on cylindrical grinding machines; guide bars must be surface ground with alundum grinding wheels; steel car-wheel treads and flanges sometimes are ground with alundum wheels, and manganese-steel frogs and switches have to be surfaced and fitted with grinding wheels composed of aluminous abrasive.

The optical industry uses aluminous abrasive wheels for lens grinding, and aluminous abrasive grain for roughing out lens blanks prior to polishing.

The cut-glass industry employs the artificial grinding wheel to a very large extent in cutting the intricate designs that go to make up the beauty of this ware.

The marble industry employs silicon carbide abrasives in thin wheels for sawing marble into slabs, and in thick wheels for surfacing or moulding the marble into various shapes and designs.

The final polish on marble slabs used in interior building operations is obtained by means of abrasive blocks composed of very fine grit silicon carbide or alundum abrasive, followed by putty powder.

Selection of Wheels.—The main points to consider in the selection of grinding wheels are as follows:—

Material.—High tensile strength (aluminous abrasive). Low tensile strength (carbide of silicon abrasive).

Operation.—Cylindrical; surfacing; internal; sharpening; off-hand grinding. Bench stands; floor stands; swing frames; portable; electric; pneumatic; flexible shaft.

Wheel speed; work speed; contact; condition and type of grinding machine; personal factor.

Material.—Whenever a grinding job is presented to you, the first thing to think of is the nature of the material to be ground—whether it is hard or soft, &c. If it falls under the general head of a high tensile-strength material—such as all steels and down as far as the hard grades of bronzes—then an alundum wheel of some kind should be used. If, on the other hand, the material falls in the class of low tensile-strength materials—such as cast-iron, chilled iron, brass, soft bronzes, aluminium, and copper—then you should use crystolon wheels.

Operation.—The next thing to consider is the nature of the operation to be performed by grinding; that is, whether cylindrical, surface, internal, sharpening, or off-hand grinding is demanded.

There are so many small points to be considered in connection with each operation that it is impossible to go into this in detail.

Wheel Speed.—Wheel speed should be considered, but with any given class of grinding it is more or less fixed. We recommend the following speeds for different classes of grinding:

Application	Speed in feet per minute
Cylindrical grinding	5500 to 6500
Snagging and general off-hand grinding on bench and floor stands	5000 to 6000
Surface grinding	4000 to 5000
Knife grinding	3500 to 4000
Hemming cylinders	2100 to 2400
Wet tool grinders	4000 to 5000
Vertical surface grinding machines	4000 to 4500
Elastic and rubber cut-off wheels	9000 to 12000

If the speeds deviate very much from these, and it is impossible to change them to suit our recommendations, then this must be taken into account in your recommendations. Speeds higher than those recommended call for slightly softer grades to offset the harder cutting action; and speeds lower than those recommended call for slightly harder grades than would be ordinarily supplied.

Work Speed.—It is impossible to tell a customer the exact speed at which his work should be done on any given grinding job. It is largely a matter of experiment. The work speed should be suited to the wheel in use and the nature of the material to be ground. On the Norton cylindrical grinder, a speed of from 60 to 80 surface feet per minute is often used for roughing and from 30 to 40 surface feet per minute for finishing. On most types of precision grinding machines, it is customary to rough grind at a higher surface speed of work than on finish grinding.

Contact.—Contact affects grade selection. Broad contact calls for softer grades and narrow contact for harder grades, as the case may be. This is especially true in snagging and off-hand grinding. Where wheels are used for grinding the burr left by welding, or for grinding sharp fins from castings, extremely hard grades, such as S, T and U, are called for. In cylindrical grinding, the contact varies with the diameter of the wheel and the work, increasing with larger work or with a larger wheel, and thus making a softer grade of wheel desirable.

Condition of Grinding Machine.—This is something which you would really have to observe personally in order to understand how it would affect grinding wheel selection. If the spindle is loose and cannot be put in good condition, a harder grade of wheel must be used than would ordinarily be recommended. This is in order to overcome the tendency to pound the wheel face to pieces. Light, flimsy machines and machines improperly secured to the foundation also call for harder grades than would ordinarily be used. Machines are frequently placed in the middle of a wooden floor which vibrates badly and in this case harder wheels must be used than for a machine on a firm, solid foundation.

Personal Factor.—This is extremely important in the operation of grinding wheels, frequently influencing the results obtained as much as 100 per cent. We mean by this that different men working on the same kind of machines and on the same work in the same shop will get one result, say 15 hours' life, whereas other men under exactly the same conditions might get 30 hours. This is based on records obtained and not on impressions, and explains why the same wheels will work differently in different shops.

(In the original, several woodcuts are given, illustrating the various apparatus, &c.).

NOTE ON BRANNERITE.*

By ROGER C. WELLS, Ph.D., U.S. Geological Survey.

THE mineral brannerite described in a recent paper in the JOURNAL OF THE FRANKLIN INSTITUTE and CHEMICAL NEWS, CXX., was carefully tested for helium, as it was expected that a mineral consisting of nearly 50 per cent of the oxides of uranium, and also containing thorium, should show at least a trace of helium. None was found, however, by the method employed. It was found that some sulphur dioxide was produced by reaction of the mineral and sodium bisulphate, and after removing this with a solution of sodium hydroxide, the remaining gas did not show the characteristic yellow line of the helium spectrum. Shortly after the paper was published the advantages of purifying the evolved gases by means of charcoal and liquid air were brought to the attention of the writer by Dr. R. B. Moore, of the Bureau of Mines, and it seemed desirable to repeat the test, using this method. Some highly active charcoal was kindly furnished by Prof. A. B. Lamb, of the Fixed Nitrogen Research Laboratory, American University, for the purpose. The clean-up of the gas by this method gave a decisive result indicating the presence of helium, which places the mineral in the list of uranium minerals in which helium has been identified. The test was conducted as follows:—

About 5 grms. of brannerite was powdered and mixed with previously fused sodium bisulphate in a hard glass tube which was connected by a thick rubber tube to the Töpler pump. Between the hard glass tube and the pump were three stopcocks, and between the latter were sealed the tube containing the charcoal and a spectrum tube, respectively. The system was evacuated until a pressure of about 0.05 mm. was permanently obtained while the charcoal was heated. The spectrum tube and pump were then cut off, leaving the stopcock between the charcoal and mineral open while the bisulphate was gently fused. The tube of charcoal was then allowed to stand in liquid air for about half an hour to effect a clean-up of the gas. Finally the gas was admitted to the spectrum tube and a little later the tube was sealed off.

The yellow helium line showed up strongly in the spectrum, and several other lines believed to belong to helium were noted. These observations were made with a spectroscope having an illuminated scale and the wave-lengths were read from a curve based on some familiar flame spectra. The method does not give more than three

significant figures. The values found ascribed to helium were 6660, 5880 (yellow line), 5030, 4720, and 4470. Two lines, 6545 and 4870, may represent hydrogen, whereas 6070, 5620, and 5200 are believed to belong to carbon. Among other lines noted but not placed are 5470 and 7000. The spectrum may be examined more carefully later if it should appear desirable, but the first object in view was to establish the presence of helium.

At the conclusion of the experiment it was found that approximately half of the mineral taken was decomposed by the short fusion with the bisulphate.

PROSPECTS OF CEREAL CROPS AND OF SUPPLY.

ACCORDING to the June *Bulletin* of Agricultural and Commercial Statistics, just published by the International Institute of Agriculture, the official estimate of the winter wheat crop of the United States of 1920 is for about 13.7 million tons and that of the spring crop for about 7.5 millions. Hence the aggregate yield of wheat in the United States will be 21.2 million tons, or 27 per cent below that of last year, though only 4.9 per cent less than the average of the five years 1914 to 1918.

It should, however, be remembered that the actual quantity exported from the United States during the current season falls short of the available surplus, so that stocks at the end of this period will be greater than those held last year.

Canada reports an area under wheat 17 per cent above the average from 1914 to 1918 also an excellent crop prospect, and it is therefore permissible to estimate that the yield will be equal to the average of the period mentioned, and much larger than it was in 1919.

On the basis of these statements, it is reasonable to expect that the North American exportable surplus of wheat for the season 1920-21 will be larger than the exports during that of 1919-20.

Government control of wheat ceased in the United States on June 1.

Crop conditions for wheat are favourable in Germany, Bulgaria, France, England, Wales, Ireland, Luxemburg, Sweden, Egypt, and average in Scotland, Italy, Poland, Switzerland, and Czecho-Slovakia. In Hungary injury has occurred owing to the great heat in May.

The estimates of the recent wheat crops in British India have been increased from 9.9 million tons to 10.2 millions, and the new season is reported as developing normally.

The rye crops are favourably mentioned in France, Sweden and Switzerland, as in average condition in Germany, Italy, and Luxemburg, and as poor in Poland and Czecho-Slovakia.

Vines and olives promise well in Italy.

Rome, June, 1920.

NOTICES OF BOOKS.

The Letters of Berzelius. III. (Published in the name of the Swedish Royal Academy of Science). By H. G. SODERBAUM. 1920. Upsala: Almqvist and Wiksels.

THIS collection of letters, written between 1809 and 1847, contains the correspondence of Berzelius

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with scholars of different nationalities, as well as their replies to him, wherever it has been possible to find them. But the letters given only deal with subjects of scientific interest. Berzelius, in his youth acquired the habit of speaking and writing in French, which habit was more strongly developed owing to his long sojourn in France, in 1818-1819, and to the fact that he moved with the diplomatic circles in the capital of Sweden. On account of this, Berzelius conducted all his correspondence in French.

Among those whose letters are included in the above collection are Goethe, Dana, Wollaston Dumas, Gay-Lussac, Fischer, &c.

The editor is to be congratulated on the care that he has taken in gathering these letters, which must have involved considerable labour and patience. The book is interspersed with photographs of eminent scientists, whose correspondence with Berzelius is included.

NOTES.

ROYAL INSTITUTION.—A General Meeting of the Members of the Royal Institution was held on July 5; Sir James Crichton-Browne, Treasurer and Vice-President in the Chair. The Chairman announced that the Institution had received a legacy of £5,000 from the late Dr. Rudolph Messel, who was a Member for 30 years. The death of Professor Auguste Righi, an Honorary Member, was reported and a resolution of condolence with the relatives was passed. Mr. A. E. Butler, Mrs. R. de l'Hopital, and Dr. W. A. M. Smart were elected Members.

APPOINTMENT.—Professor Sir John Cadman, K.C.M.G., D.Sc., University of Birmingham, Mr. W. B. Hardy, Soc. R.S., Gonville and Caius College, Cambridge, and Professor Sydney Young, D.Sc., F.R.S., Trinity College, Dublin, have been appointed by an Order of Council dated June 24, 1920, to be members of the Advisory Council to the Committee of the Privy Council for Scientific and Industrial Research.

COMMEMORATION DAY AT LIVINGSTONE COLLEGE.—A very successful Commemoration Day, the first for five years, was held at Livingstone College, Leyton, on Friday, June 25. A large number of guests were present, including the Lord Bishop of Chelmsford, who occupied the Chair, the Bishop of Bendigo, the Bishop of Honduras, the Chaplain-General of the Forces, Mr. R. L. Barclay (Treasurer of the College), Dr. and Mrs. C. F. Harford (Founders of the College). At the meeting held in the grounds, after prayer led by Bishop Taylor Smith, a short statement was made by the Principal. Speeches were given by three former students of the College, Rev. J. Kerswell, of the Primitive Methodist Missionary Society, Mr. W. H. Soamell, of the Church Missionary Society, and Mr. R. A. Lorrain, of the Lakher Pioneer Mission. With many interesting anecdotes each missionary spoke of the great debt he owed to Livingstone College as regards his own

health and also in the help it had been in his missionary work; they told of many lives which have been saved through the use of their knowledge gained at Livingstone College, in cases where there was no qualified doctor near, and of the opportunities which this medical work gave for furthering their work as missionaries of the Gospel. They emphasised the necessity of all missionaries receiving such training before being sent abroad. The Bishop of Chelmsford spoke of his long connection with the College in many ways. He felt that there never was a time when it was more important for English people to realise their responsibilities with regard to the mission field; missionary work was a point on which he felt very strongly. When he looked at Livingstone College he thought of it as deserving the title of a "Workers' Life Preservation College." "Think," he said, "of the deplorable loss of life on the part of missionaries. Think of the time, cost, and trouble of sending a man out thousands of miles and then perhaps to die within a month or even a week of his arrival, from what could be called largely preventable causes." He believed that through the knowledge gained at Livingstone College the lives of many missionaries could be saved and they would do much useful work. "The Government realised during the last war the value of proper medical attention being given to our men; the Church must take just as great pains to ensure the preservation of the life of her workers as the Government does of hers." He spoke of the unity in missionary work which the College was instrumental in advancing and said the College might also be called "A Preparation School for Re-union." He referred to the fact which had previously been mentioned, the large number of nations represented amongst the students of the College, in virtue of which the College might also be called "A Preparation School for the League of Nations." He ventured therefore from every point of view to advocate the claims of Livingstone College, which he believed to be worthy of the name of Livingstone, and he appealed to all to support it by sending students, by financial help and by prayer, in order to enable it to efficiently carry on its work, which he felt was so necessary to the missionary cause.

DETERMINATION OF MERCURY.—C. M. Bouton and L. H. Duschak (*Journ. Frank. Inst.*).—The volumetric methods for the determination of mercury described in the literature permit the selection of a variation of about 1 mgrm. of Hg. or within 0.1 per cent on a 1-grm. sample. As much of the world's supply of the metal is obtained from ores carrying less than 1 per cent mercury, a method that will quickly and accurately determine a variation of less than 1 mgrm. Hg is greatly to be desired. Of the numerous methods tested by the investigators of the Berkeley, Calif., stations of the Bureau of Mines in connection with a study of mercury condenser losses, the method of titration with potassium thiocyanate, using ferric sulphate or nitrate as an indicator, proved to be the only one capable of the desired refinement. The titration is vitiated by the presence of any halide; therefore, in bringing the sample into solution, a method must be employed which absolutely excludes all halogen compounds. With slight modification, the method can be applied to

the determination of mercury in practically any material, including that containing considerable quantities of organic matter. Details as to the equipment used, analytical procedure, the modifications necessary when organic matter or much sulphur is present, procedure for assaying a filtered precipitate, alternative procedure for refractory samples; and the results of experimental determination of distillation procedure, effects of evolution of gas, possibility of retention of mercury by the charge, trial assay with sulphur and organic matter present, interfering elements, and titration are given in Technical Paper 227 of the Bureau of Mines. With readily provided facilities one operator can make 50 to 60 determinations in an eight-hour day, exclusive of the time required for preparing the sample. Technical Paper 227 also includes a bibliography on analytical methods for the determination of mercury.

NOTICE.

OWING to the greatly increased cost of printing and paper, and the advance in the postal rates, we have been compelled to raise the price of the **CHEMICAL NEWS** from 4d. to 6d. (by post 7d.). The new subscription rates are as follows:—

Yearly (52 Nos.)	- - -	£1 12 0
Half yearly (26 Nos.)	- - -	£0 16 0
Quarterly (13 Nos.)	- - -	£0 8 0

NOTICE OF REMOVAL.

On Friday, July 9, 1920, the Publishing and Editorial Offices at 16, Newcastle Street will be closed for the purpose of removing to

97, SHOE LANE, LONDON, E.C. 4;
which will be opened for business at 10 a.m. on Monday, July 12.

NOTICES.

EDITORIAL.—All Literary communications, and Books, Chemical Apparatus, &c., for review or notice to be addressed to the **EDITOR**.

SUBSCRIPTIONS, £1 12s per annum, payable in advance, should be addressed to the **MANAGER**.

BACK NUMBERS and VOLUMES can be purchased on application to the **MANAGER**.

THE CHEMICAL NEWS,
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ADVERTISEMENTS.

All communications for this Department should be addressed to—

T. G. SCOTT & SON,
63, LUDGATE HILL, LONDON, E.C. 4.

UNIVERSITY OF MANCHESTER, DEPARTMENT OF CHEMISTRY.

Applications are invited to fill the following Positions on the Chemical Staff:—

- (1) A **READER or SENIOR LECTURER IN ORGANIC CHEMISTRY**, or, alternatively, **LECTURER IN ORGANIC CHEMISTRY**.
- (2) A **LECTURER IN INORGANIC AND PHYSICAL CHEMISTRY**.
- (3) Three **ASSISTANT LECTURERS IN CHEMISTRY**.

Applications should be forwarded, not later than **JULY 15** next, to the **REGISTRAR**, from whom detailed conditions may be obtained.

BIRMINGHAM MUNICIPAL TECHNICAL SCHOOL.

Principal—W. E. SUMPNER, D.Sc.

Applications are invited for the **HEADSHIP OF THE CHEMICAL DEPARTMENT**, now vacant by the appointment of Dr. T. S. PRICE as Director of Research to the British Photographic Research Association.

Full particulars of the appointment can be obtained from the **SECRETARY**, Municipal Technical School, Suffolk Street, Birmingham.

ASSISTANT CHEMISTS wanted at once for the Admiralty Inspection Laboratories at Holton Heath. Candidates must have a qualification equivalent to that of the Associateship of the Institute of Chemistry, and must possess a sound knowledge of Technical Analysis, preferably explosives.

The posts are non-pensionable and the salary is subject to bonus, the present value of the commencing salary being £319, rising by £16 annually to £412.

Applications, stating qualifications and experience, should be made by letter to the **INSPECTOR OF NAVAL ORDNANCE**, Holton Heath, near Wareham, Dorset.

Wanted, well-trained LABORATORY AND LECTURE ROOM ASSISTANT to take charge in the Chemical Department, McGill University, Montreal, Canada. Duties: Distribution and ordering of Supplies and Apparatus, setting up Lecture Apparatus, simple Repairs, &c. Must be experienced, steady, and have mechanical ability. Wages 30 dollars per week. Duties begin September 15.—Apply, with references and qualifications, to G. S. WHITBY, 8, Victoria Avenue, Hull, Yorkshire, before August 10.

A JUNIOR of either sex with some knowledge of Chemistry, and commercial experience in chemical analysis, is required for a junior position in the Laboratory of a large Chemical Works. Kindly state salary required to Box 103, c/o Scott & Son, 63, Ludgate Hill, London, E.C. 4.

TWO JUNIOR ASSISTANT CHEMISTS wanted for laboratory in Newcastle-on-Tyne. Those having experience in analysis of non-ferrous metals and alloys preferred. Reply stating age, experience, and salary required to Box 804, c/o Scott & Son, 63, Ludgate Hill, London, E.C. 4.

THE CHEMICAL NEWS.

VOL. CXXI., No. 3144.

SOME SOFT WATERS OF CENTRAL NEW YORK.

By J. B. SHUMAKER and NICHOLAS KNIGHT.

1. THE water here described is from a well in the town of Sangerfield, Oneida County, New York, about a mile-and-a-half south of the village of Waterville. It is on the flat land in the bottom of the Sangerfield valley, near the head waters of the Chenango River.

The well is forty-three feet in depth and was sunk in the early '80's. The top soil of the land in the locality is a clay loam, and in boring the well the first twenty-seven feet encountered was hard clay, underneath which was a dark coarse sand, entirely different from any other formation in the neighbourhood. It is an artesian well and flows continuously. The summer and winter temperature of the water is practically constant. The figures express the amounts of the different substances in a million parts of the water.

Total solid residue	188.20
SiO ₂	13.20
Fe ₂ O ₃ and Al ₂ O ₃	3.20
CaCO ₃	113.20
CaSO ₄	4.00
MgCO ₃	42.80
NaCl and KCl	11.80
Free Ammonia	0.00
Albuminoid ammonia	0.00
Nitrogen in nitrates	0.00
Nitrogen in nitrites	0.0003

The water is pure and likewise unusually soft for the particular locality.

Dr. A. P. Brigham, Professor of Geology in Colgate University, in a private communication says: "The bedrocks in Sangerfield at any moderate depth would be sandstone or possibly shaly sandstone of the Hamilton group; but the fact is that most of the well waters and pond waters of the region are very hard owing to the amount of limestone flour which has been incorporated in the local materials of the glacial drift by moving from limestone formations that lie to the northward. However, water of a softer character is sometimes obtained from the valley bottoms under thick beds of clay."

This water affords another good illustration of how the character of the soil determines the quality of the water in the region.

Our thanks are due to Dr. Nelson O. Brooks, Physician of the Board of Health of the City of Oneida, New York, for his interest in sending us the sample of water for the analysis.

2. This is a shallow well, only twelve feet deep, also in Oneida County, New York, near Fish Creek, on the premises of James L. Bentley. It is located possibly eighteen or twenty miles from the well described in 1. The analysis is as follows:

Total solids in platinum dish ...	186.40
SiO ₂	2.60
Fe ₂ O ₃	0.00
Al ₂ O ₃	1.80
CaCO ₃	99.60
CaSO ₄	27.00
MgCO ₃	47.40
NaCl and KCl	11.80
Free ammonia	0.00
Albuminoid ammonia	0.00
Nitrogen in nitrates	0.10
Nitrogen in nitrites	0.002

The water is also pure and soft, as would be expected from the locality in which the well is located. It is in the pure white sand about a half mile distant from Oneida Lake. The water doubtless comes from the lake and so has a half mile of pure sand filter. This would easily account for its freedom from organic contamination and the absence of much material in solution.

We desire to express our thanks to J. L. Bentley for sending us this sample of water.

Cornell College, Mount Vernon, Iowa,
June 12, 1920.

VELOCITY OF SORPTION:

By ALWYN PICKLES.

(A). From Solution.

CHARCOAL dust used, 15 grms. per litre of solution. Temperature kept as nearly constant as possible and stirring done by a Heinrich mechanical stirrer. At intervals some of the mixture, charcoal-solution, removed, filtered, and concentration of filtrate determined by methods varying with solution used.

The solution became weaker in solute, rapidly at first and then more slowly. The action is a kind of mono-molecular action, so an attempt was made to apply the formula for mono-molecular reaction velocity, *i.e.*—

$$k = \frac{1}{t} \log_e \frac{a}{a-x}$$

In every case studied the values of *k* showed a continual decrease. This is due to the rapid adsorption being followed by the slower penetration effect, absorption.

Suppose total surface of the charcoal is *S*, then as sorption proceeds *S* will diminish and such diminution will be inversely proportional to amount of solute "adsorbed", *x* say.

$$\therefore S = k_1 \cdot \frac{1}{x}$$

Also, rate of removal of solute from solution varies as concentration of solution and also as surface *S* and therefore as their product.

$$\therefore \frac{dx}{dt} = (k_2(a-x) \cdot S) \\ = k_1 k_2 (a-x) \cdot \frac{1}{x}$$

By integration, if *t*=0 and *x*=0 we get—

$$K = \frac{1}{t} \left\{ \log_e \frac{a}{a-x} - 0.4343 \frac{x}{a} \right\}$$

If the time between two successive readings be denoted by *t*₂-*t*₁, the following expression may be used:—

$$K = \frac{1}{t_2 - t_1} \left\{ \log_e \frac{a-x_1}{a-x_2} - 0.4343 \frac{x_2 - x_1}{a} \right\}$$

In the following results the values of k , K , and K_1 , are obtained by converting logarithms to base 10.

Case i. *Benzoic Acid*.—N/10 in aqueous alcohol. Estimation using alcoholic KOH. Temperature 14° C. Birch charcoal dust used.

t (mins.).	Per cent sorption.	k .	K .	K_1 .
1	14	0.1521	0.0121	—
2	18	0.0982	0.0082	0.0083
3	21	0.0789	0.0089	0.0091
6	28.5	0.0560	0.0085	0.0087
9	34	0.0471	0.0094	0.0075
12	38	0.0398	0.0081	0.0078
15	41.5	0.0358	0.0082	0.0078
19	44.5	0.0308	0.0074	0.0069

Case ii. *Iodine*.—In Potassium iodide N/10. Temperature 15° C. Birch charcoal dust used. Estimation using thiosulphate. The experiment also performed at higher temperatures.

t (mins.).	Per cent sorption.	k .	K .	K_1 .
1	31.6	0.379	0.063	—
3	49.4	0.227	0.062	0.064
6	62.5	0.163	0.059	0.057
9	70.0	0.134	0.057	0.049
11	74.5	0.124	0.056	0.058
13	78	0.116	0.056	0.057
15	80.5	0.109	0.053	0.049
17	83	0.104	0.052	0.058
20	84	0.092	0.050	0.017

Iodine, N/10. Temperature 25° C.—

t (mins.).	Per cent sorption.	k .	K .	K_1 .
1	35	0.429	0.079	—
2	47.2	0.318	0.082	0.085
4	59.5	0.227	0.088	0.069
7	69.7	0.171	0.072	0.062
10	75.1	0.139	0.054	0.047

Iodine, N/10. Temperature 50° C.—

t (mins.).	Per cent sorption.	k .	K .	K_1 .
1	46.9	0.632	0.163	—
2	58.5	0.440	0.148	0.130
3	69.0	0.391	0.161	0.187
5	87.1	0.409	0.235	0.348
8	100	—	—	—

Iodine, N/10. Temperature 70° C.—

t (mins.).	Per cent sorption.	k .	K .	K_1 .
1	70.6	1.229	0.523	—
2	83.2	1.16	0.744	0.456
3	94.1	0.945	0.631	0.933
4	100	—	—	—

The iodine is evidently removed from solution more rapidly but not so regularly. The solvent action of the solution becomes apparent at the higher temperatures and the penetration effect is thereby increased. Filtration was carried out as rapidly as possible and through warmed funnels.

Case iii. *Potassium Permanganate*, N/10.—Temperature 12° C. Estimation by adding 10 cc. of filtrate from charcoal (birch dust) to 10 cc. of acidified N/10 oxalic acid at about 60° C. and estimating excess acid with N/10 potassium permanganate.

Time (mins.).	Per cent sorption.	k .	K .	K_1 .
1	34	—	—	—
2	44	0.289	0.069	0.073
3½	54.75	0.244	0.066	0.086
6½	69.5	0.182	0.075	0.074
10	77.5	0.149	0.072	0.067
13	82.75	0.035	0.071	0.070
16½	87.0	0.121	0.068	0.073
20	90.5	0.118	0.072	0.074
23½	91	0.102	0.063	0.015

Potassium Permanganate, N/10. Temperature 25° C.

Time (mins.).	Per cent sorption.	k .	K .	K_1 .
1	43	0.56	0.13	—
2	47.25	0.321	0.085	0.0343
3½	55	0.228	0.071	0.0457
6	69.5	0.198	0.082	0.0970
9	79.75	0.176	0.087	0.1015
12	90.0	0.191	0.116	0.1983

Potassium Permanganate, N/10. Temperature, 50° C.

Time (mins.).	Per cent sorption.	k .	K .	K_1 .
1	44.5	0.586	0.141	—
2	51.0	0.356	0.101	0.057
3½	60.25	0.264	0.92	0.076
6	74.5	0.227	0.103	0.124
9	87.0	0.237	0.140	0.183
12	100	—	—	—

Potassium Permanganate, N/10. Temperature, 70° C.—

Time (mins.).	Per cent sorption.	k .	K .	K_1 .
1	46	0.616	0.156	—
2	61	0.470	0.165	0.172
3½	74.75	0.390	0.177	0.195
6	87.5	0.346	0.200	0.234
9	100	—	—	—

The variation in the value of K and K_1 is due to three factors:—

- Decomposition of permanganate through catalytic effect of charcoal.
- Solvent action of the solution in opening up charcoal capillaries.
- Reducing effect of charcoal.

It is well known that hot permanganate solutions are unstable and a substance like charcoal would facilitate decomposition.

With increase in concentration of solution more solute is removed absolutely but not so relatively.

Benzoic Acid, N/8. $T=14^\circ$ C. Birch charcoal dust as before—

t (mins.).	Per cent sorption.	k .	K .
1	16.2	0.174	0.012
3	23.5	0.090	0.012
6	33.8	0.069	0.013

Potassium Permanganate, 4 grms. per litre. $T=14^\circ$ C. Birch charcoal dust as before—

t (mins.).	Per cent sorption.	k .	K .
1	39.8	0.506	0.108
2	49.8	0.344	0.095
3	60.1	0.306	0.106
6	68.4	0.193	0.079

At concentrations above N/10 potassium permanganate was removed irregularly by the charcoal. Also, at higher temperatures decomposition became considerable.

Coarse charcoals were found unsuitable for velocity investigation.

Animal charcoal gave a very rapid adsorption effect, this being followed by a slow and irregular absorption effect.

(B). *Velocity of Sorbtion of Gases.*

The gases used were NH_3 and HCl . Air was slowly aspirated through strong ammonia and strong hydrochloric acid respectively and the gases dried before being passed over the charcoal.

The amount of NH_3 adsorbed by a given weight of charcoal was determined by adding the charcoal, after adsorption, to a known excess of standard sulphuric acid. After standing half an hour the charcoal was filtered off and washed and the amount of acid remaining in filtrate and washings determined by using standard caustic soda.

The HCl adsorbed was determined by adding to a known excess of standard NaOH , the un-neutralised NaOH being estimated by a standard acid.

The charcoals used were heated for a short time before use and cooled in as high a vacuum as possible (20 cc. of mercury). This process releases adsorbed air and possibly contained hydrocarbons, thus rendering more surface available for adsorption.

I. *Cocoanut Charcoal, Ammonia.* $T=13^\circ \text{C}$.
Time (mins.) 1 2 3 4 6 9 15
Vol. of NH_3 at N.T.P. per cc. charcoal 10.8 18.9 24 27.3 32.1 37 41.1

After 60 minutes 68.3 cc. adsorbed.

II. *Cocoanut Charcoal, HCl.* $T=13^\circ \text{C}$.—
Time (mins.) ... 1 2 3 4 6 9
Vol. HCl per cc. charcoal ... 3.9 7.0 10.0 13.2 17.6 23.1

After an hour 46.3 cc. adsorbed.

The rate at which NH_3 is taken in slows down much sooner than in the case of HCl . Possibly in presence of traces of moisture, the acid has a solvent effect and so opens up fresh surface in the charcoal as penetration proceeds.

Adsorption is usually very rapid, but in these cases very little gas was adsorbed during the first minute. This may be due to the adsorbed air not being properly driven out before admitting the gases in question. Accurate estimation was also found to be difficult.

Further work is being done on this question. The values of k and K are given:—

I. Ammonia.

k .	K .
0.144	0.027
0.128	0.028
0.106	0.028
0.086	0.026
0.061	0.021

II. HCl.

k .	K .
0.086	0.0020
0.083	0.0074
0.081	0.0090
0.084	0.0127
0.079	0.0160

The values are calculated assuming $a=68.3$ and 46.3 cc. respectively. Those for HCl seem to show that fresh surface is continually being opened up. In the case of ammonia the values of K are so nearly constant as to suggest that 68.3 is the true capacity per cc. of the charcoal for ammonia under these particular conditions.

When a charcoal charged with ammonia is placed in acid most of the ammonia is neutralised at once. This is the adsorbed gas. The charcoal, if rapidly removed from the acid, soon smells of ammonia. This is due to release of absorbed gas. Charcoal charged with HCl behaves

similarly in presence of alkali. This effect depends on the kind of charcoal and on its state of division—the larger the particles the greater the secondary effect.

THE POROSITY AND VOLUME CHANGES OF CLAY FIREBRICKS AT FURNACE TEMPERATURES.*

By GEORGE A. LOOMIS.

THIS paper deals with the permanent changes in porosity and volume of clay fire-bricks when re-burned to temperatures at or above those to which they were originally fired. These were measured for a series of temperatures to determine what relation, if any, might exist between these changes and the deformation of the same bricks under load at furnace temperatures. The possibility of such a relation is suggested by the fact that contraction of clay on heating and decrease in porosity are, to a certain extent, indications of the amount of softening of the mass due to the action of fluxes present and hence indicative of decreased resistance to deformation under pressure or decreased viscosity. Softening point determinations were also made to determine what relations these might bear to the results of the load test.

The results of tests on a large number of clay fire-bricks from various parts of the country show that bricks which withstand a load test of 40 pounds per square inch at 1350°C . without marked deformation show no marked changes in porosity or volume up to 1425°C . Bricks which do not withstand the test generally show appreciable contraction or expansion, accompanied by considerable decrease in porosity. Bricks which showed overburning and the development of vesicular structure below 1425°C ., by marked expansion or increase in porosity, invariably failed under load. In general, bricks which show a decrease in porosity exceeding 5 per cent or a volume change exceeding 3 per cent (amounting to approximately 1 per cent in linear dimensions) when refired to 1400°C . fail to pass the load test.

No definite relation could be determined between the softening point of a brick and its ability to withstand pressure at high temperature. All bricks softening below cone 28 failed completely in the load test. Some showing quite high softening points also failed, probably due to the use of an inferior bond clay in the mixture or too small an amount of bonding material.—*Journal Franklin Institute*, June, 1920.

* Abstract of *Technologic Paper No. 159*, U.S. Bureau of Standards.

CAFFEINE FROM COFFEE SOOT.

SUGGESTION FOR RECLAIMING A PORTION OF THE CONSTITUENTS WHICH ARE VOLATILISED IN THE ROASTING PROCESS.

By GEORGE E. ÉWE, Philadelphia, Pa.

THE soot which collects in the flues and on the upper and inner surface of coffee roasters frequently contains enough caffeine to warrant its use as a raw material for the production of this valuable substance. Since there is a considerable demand for caffeine, the collection of coffee soot,

if established upon a profitable basis, would result in an added source of income to coffee roasting firms.

In order to interest roasters in the collection of the "soot," a statement regarding the probable price which might be obtained for it is pertinent. No market price has been thoroughly established for this article, because it varies greatly in caffeine content. Specimens recently examined in the Pharmaceutical Research Laboratories of the H. K. Mulford Co., Philadelphia, ranged all the way from 0.08 to 22.2 per cent in caffeine content.

Some Analyses of Coffee Soot.

Sample No.	Caffeine content. Per cent.	Source of sample (a).
1	22.20	Flue of roaster.
2	18.30	Flue of roaster.
3	11.94	Inner walls of roaster.
4	3.25	Ceiling of roaster.
5	1.76	Dust collector on roof (mixed with chaff).
6	0.70	Flue of roaster.
7	4.18	Flue of roaster.
8	1.20	Flue of roaster.
9	7.10	Flue of roaster.
10	11.20	Flue of roaster.
12	0.08	Flue of roaster.
13	4.42	Ceiling of roasting room.
14	15.30	Flue of roaster.

(a) None of the commercial roasters from which these samples were obtained, were equipped with collectors for the express purpose of collecting the "soot," and only one (No. 5) was equipped with a dust collector.

Since tea fluff, tea siftings, and damaged tea, which contain from 1 to 5 per cent of caffeine, are commonly used raw materials for the production of caffeine, it is evident that collections of coffee soot with similar caffeine contents would be excellent material for the production of caffeine and should command a price approximately equal to that of these tea materials. These tea materials were quoted around 10 cents per lb. during December, 1919. It is encouraging to report here that one-half of the coffee soot samples which we have examined possessed caffeine contents which were well above the maximum content of the starting materials obtained from tea.

A statement regarding the probable amount of soot collectable from roasters in a given time would also be pertinent, but unfortunately this cannot be offered, for the reason that no commercial roaster equipped with a soot collector was met with in this investigation. Only a properly designed and properly operated soot collector will yield figures for this.

By coffee soot is meant the smoke-like vapour which arises from the roasting barrel during the roasting process. Coffee chaff, which is also a by-product of the roasting of coffee, also contains caffeine, but its economic use for the production of caffeine has not been rendered possible up to the present time. It contains much smaller proportions of caffeine than the raw materials from tea, and in addition contains considerable pyro-ligneous or tarry matter which makes the production of pure white caffeine very difficult and expensive. Specimens of coffee chaff recently examined in the Mulford laboratories ranged between 0.6 and 1.1 per cent in caffeine content.

Methods of collecting Coffee Soot.

Caffeine is a sublimable substance, that is, it can be made to pass into the form of a vapour by heat; and upon cooling this vapour, the caffeine will be precipitated as a crystalline "snow." It is by the principle of sublimation that caffeine is collected; since the utilisable constituent of coffee soot and flue gases from the roasting of coffee is caffeine, it is by sublimation that the caffeine containing coffee soot is best collected.

Coffee soot escapes from the roaster *via* the flue. In practice, a considerable proportion also escapes into the room in which the roaster is situated, and where the collection of the soot is made a practice for profit, it is a source of loss of income. This loss can be prevented by proper regulation of the draught in the flue as described later in this article. Since coffee soot escapes *via* the flue, it is necessary, therefore, to connect the collector with the flue. Theoretically, the conditions required are a means of cooling the coffee soot and flue gases to precipitate the caffeine contained in them; a collector to retain the precipitated caffeine and soot; and a draught regulator to control the rate of flow of the soot and gases through the collector so that it is not so fast that caffeine passes through the collector and is lost in the outer air, nor so slow that the soot is lost by being forced out into the air of the room in which the roaster is situated.

Details of a Coffee Soot Collector.

The collector consists of a water-jacketed, sheet-iron or cast-iron box equipped with baffle plates arranged so as to make a tortuous path for the soot from the coffee-roaster. It is connected in an upright position with the flue of the roaster.

If the resistance of the baffle plates is too great to permit the passage of the soot and flue gases, an electric fan must be installed in the exit pipe of the collector. The suction thus created must be just enough to prevent the soot and gases from coming out into the room in which the roaster is situated, and not enough to carry any of the chaff up into the collector.

The water jacket is required to be operated only in the summer, and may not be necessary at all in connection with smaller roasters.

The glass windows with incandescent lamps before them, in the sides of the collector, are required during the installation of the collector when the best conditions for operation are being established.

The door of the collector is attached very loosely so as to allow a final tight adjustment by means of the four screw clamps. A soot-tight joint is obtained by means of an asbestos or composition gasket fixed in a slot around the inner edge of the door.

The interior of the collector is painted with aluminium paint, to prevent rust from forming and becoming mixed with the soot.

The collected soot is removed by releasing the screw clamps, throwing back the door on its hinges and scraping out the soot with a long steel or wooden blade.

Only the soot, and not the chaff, possesses any degree of commercial value, therefore the collector will probably not be applicable to the collection of soot from the type of roaster in the flue of which a strong blower must be employed, for the reason that the chaff and soot are usually in-

separably mixed by the blower. The collector can be applied to the collection of soot from a roaster equipped with a blower by reducing the speed of the blower, so that none of the chaff is blown up into the collector, the speed of the blower being only enough to prevent the escape of soot and flue gases into the room in which the roaster is situated. If the purpose of the blower is the removal of the chaff, reduction of its speed to collect the soot will nullify this purpose and add an operation to the roasting process, namely the removal of the chaff. This will increase the expense of coffee-roasting process, and should be debited against the returns to be expected from the collection of the soot.

For either Gas or Coal Roasters.

The collector is applicable to the collection of coffee soot from either gas-fired or coal-fired roasters, but it must be remembered that coal soot or gas soot have no value, and therefore efforts must not be directed toward the production of these types of soot.

No dimensions are indicated in the drawing of the collector, as any size can be used according to requirements; merely keeping the dimensions in approximately the same ratio as they appear in the drawing. For a single roaster, it is likely that a collector 6 feet in height will completely collect the soot.

To the writer's knowledge the collection of coffee soot is not being practised in this country, but is in Continental European countries with reputed satisfactory returns. The Continental preference for more thoroughly roasted coffee may be a factor in this respect, because the soot would consequently be richer in caffeine. Whether coffee soot can be established as a profitable source of caffeine in this country is problematical and is a challenge to our best efforts.—*Tea and Coffee Trade Journal*, March, 1920.

THE STRUCTURE OF ATOMS AND ITS BEARING ON CHEMICAL VALENCE.*

By IRVING LANGMUIR.

ACCORDING to the well-established Rutherford-Bohr theory, all the positive electricity in an atom is concentrated in a *nucleus* at its centre. The dimensions of this nucleus are negligibly small compared with those of the rest of the atom, its diameter being of the order of 0.00001 of that of the atom. The charge on the nucleus is an integral multiple of the charge of an electron, but, of course, opposite in sign. The remainder of this atom consists of electrons arranged in space about the nucleus, the normal number of such electrons (called the *atomic number*) being equal to the number of unit positive charges on the nucleus, so that the atom as a whole is electrically neutral. If the number of electrons in the atom exceeds the atomic number we have a negatively charged atom or ion, while in the reverse case a positively charged atom or ion results. The atomic number of any element has been found to be equal to the ordinal number of the element in the periodic table. Thus hydrogen has the atomic number 1, helium 2, lithium 3, carbon 6, neon 10, chlorine 17, nickel 28, silver 47, cerium 58, tung-

sten 74, radium 88, and uranium 92. The atomic numbers can be determined experimentally from the X-ray spectrum, so that we are not dependent upon the periodic table for our knowledge of these numbers.

Bohr, Sommerfeld, and others have developed an extensive and very successful theory of spectra upon the hypothesis that the electrons in atoms are in rapid rotation in plane orbits about the nucleus in much the same way as the planets revolve around the sun. Stark, Parson, and G. N. Lewis, on the other hand, starting from chemical evidence, have assumed that the electrons are stationary in position. It should be noted that Bohr's theory has had its greatest success when applied to atoms or ions containing only one electron and that it seems incapable of explaining the chemical or ordinary physical properties of even such simple elements as lithium, carbon, or neon.

The two theories can, however, be reconciled if we consider that the electrons, as a result of forces which they exert on one another, rotate about certain definite positions in the atom which are distributed symmetrically in three dimensions. Thus for atoms containing only a single electron the chemical theory is in agreement with Bohr's theory. But for an atom such as neon the eight electrons in the outside layer would revolve around positions which are located about the nucleus in the same way that the eight corners of a cube are arranged about the centre of the cube. This structure is not inconsistent with those parts of Bohr's theory which have received experimental confirmation. In fact, Born and Landé (*Verh. d. phys. Ges.*, 1918, xx., 210) starting with Bohr's theory and without knowledge of Lewis' work, arrived at exactly this conception of the structure of atoms (*i.e.*, the cubic atom) from a study of the compressibility of the salts of the alkali metals.

The atomic numbers and the properties of the inert gases furnish us with a clue to the arrangement of the electrons within atoms. The low boiling point, the high ionizing potential, the chemical inertness, &c., of helium prove that the arrangement of the electrons in the helium atom is more stable than that in any other atom. Since this atom contains two electrons we must conclude that a pair of electrons in the presence of a nucleus represents a very stable group. It is reasonable that with elements of higher atomic numbers there should be an even greater tendency for this stable pair of electrons to form about the nucleus. There are two sets of facts which furnish conclusive experimental evidence that this stable pair exists in all atoms above helium.

In the first place, the properties of lithium, beryllium, &c., show that in these elements also the first two electrons are held firmly while the remainder are easily detached. Thus, lithium readily forms a univalent positive ion by the detachment of one of the three electrons in its neutral atom. The divalence and other properties of beryllium prove that there is little or no tendency for a second stable pair of electrons to surround the first pair.

In the second place, the absence of irregularities in the observed K and L series of the X-ray spectra of the various elements proves that there are no sudden changes in the number of electrons in the innermost layers of electrons about the nucleus. From these two sets of facts, as well as

* From the *Journ. of Indus. and Eng. Chem.*, April, 1920.

from other evidence, we may take it as a fundamental principle that the arrangement of the inner electrons undergo no change as we pass from elements of smaller to those of higher atomic number.

The properties of neon indicate that its atoms are more stable than those of any other element except helium. Since the atomic number is 10, and the first two electrons form a stable pair about the nucleus as in the helium atom, it follows directly that the other eight electrons arrange themselves in a second layer or shell possessing a very high stability. If these eight electrons revolved about the nucleus in a single circular orbit or ring, as would be suggested by Bohr's theory, there is no apparent reason why there should be any very great difference in stability between rings having 7, 8 or 9 electrons. On the other hand, we readily see that the geometrical symmetry of the arrangement of the 8 electrons at (or rotating about) the 8 corners of a cube would not only account for a high degree of stability but for the fact that an arrangement of 7 or 9 electrons would have no such stability. Chemical considerations and Born and Landé's work on compressibility also lead us to this spatial arrangement of the electrons. We shall refer to the stable group of 8 electrons by the term *octet*. From the principles already enunciated it is clear that in the atoms of all the elements above neon the inner electrons are arranged in the same way as those of neon.

From the atomic numbers of the inert gases we are thus able to determine the number of electrons in the various layers or shells of electrons which exist in the atoms. The results are summarised in Table 1.

TABLE 1.—Distribution of Electron in the Various Shells.

Shell.	Number of electrons.	Inert gas corresponding to completed layer.
1st shell	$2=2 \times 1^2$	He 2
2nd shell, 1st layer ...	$8=2 \times 2^2$	Ne 10
2nd shell, 2nd layer ...	$8=2 \times 2^2$	Ar 18
3rd shell, 1st layer ...	$18=2 \times 3^2$	Kr 36
3rd shell, 2nd layer ...	$18=2 \times 3^2$	Xe 54
4th shell, 1st layer ...	$32=2 \times 4^2$	Nt 86

Thus the xenon atom with an atomic number 54 contains 54 electrons arranged as follows:—Close to the nucleus are two electrons which constitute the first shell. This is surrounded by the second shell which contains two "layers" of 8 electrons each. The third shell, which in the xenon atom is the outside shell, contains 18 electrons.

An examination of the numbers of electrons in the layers (Table 1, 2nd column) shows that they bear a simple mathematical relation to each other, namely, that they are proportional to the squares of the successive integers 1, 2, 3, and 4. This is to be looked upon as perhaps the most fundamental fact underlying the periodic arrangement of the elements. It is significant that in Bohr's theory these same numbers, 1, 4, 9, 16, &c., play a prominent part. Thus the energies of the electron in the various "stationary states" are proportional to $1, 1/4, 1/9, 1/16, \&c.$, and the diameters of the various possible orbits in Bohr's theory are proportional to 1, 4, 9, 16, &c. In Bohr's theory the various stationary states correspond to different number of quanta (Planck's quantum theory), the innermost orbit corresponding to one

quantum, the second orbit to two quanta, &c. We should thus consider (Table 1) that the electrons in the 1st shell are monoquantic, those in both layers of the 2nd shell are diquantic, &c. It is interesting that Born and Landé, from quite other evidence, have concluded that the outermost electrons of the chlorine atom (2nd layer of the 2nd shell) are diquantic instead of triquantic, as was at first assumed.

The foregoing theory of the arrangement of electrons in atoms explains the general features of the entire periodic system of the elements and is particularly successful in accounting for the position and the properties of the so-called 8th group and the rare earth elements. It also serves to correlate the magnetic properties of the elements.

Let us now consider the bearing of this theory of atomic structure on the phenomena of chemical valence. The outstanding feature of the theory is that there are certain groups of electrons, such as the pair in the first shell and the octet in the second, that have a remarkable stability. Those atoms in which all the electrons form parts of such stable groups (*viz.*, the inert gases) will have no tendency to change the arrangement of their electrons and will thus not undergo chemical change. Suppose, however, we bring together an atom of fluorine ($N=9$) and an atom of sodium ($N=11$). (We will denote the atomic number of an element by N .) Ten electrons are needed for the stable pair in the first shell and the octet in the second shell, as in the neon atom. The sodium atom has one more electron than is needed to give this stable structure while the fluorine atom has one electron too few. It is obvious then that the extra electron of the sodium atom should pass over *completely* to the fluorine atom. This leaves the sodium atom with a single positive charge while the fluorine becomes negatively charged. If the two charged atoms or ions were alone in space they would be drawn together by the electrostatic force and would move as a unit and thus constitute a molecule. (It is convenient and it has been customary with many physicists to speak of a charged atom or molecule as an ion, irrespective of whether or not the particle is able to wander under the influence of an electric field. The writer has used the term in this way in his recent publications. This practice is very distasteful to many physical chemists and is apt to be misunderstood by them. Nevertheless, it seems to me probable, especially in view of the recent work of Milner and Ghosh, that it will be desirable to abandon the physical chemists' definition of the ion and to apply it to all charged atoms or molecules. The ion which wanders may then be referred to as a "free ion"). However, if other sodium and fluorine ions are brought into contact with the "molecule" they will be attracted as well as the first one was. There will result (at not too high a temperature) a space lattice consisting of alternate positive and negative ions and the "molecule" of sodium fluoride will have disappeared. Now this is just the structure which we find experimentally for sodium fluoride by Bragg's method of X-ray crystal analysis. There are no bonds linking individual pairs of atoms together. The salt is an electrolytic conductor only in so far as its ions are free to move. In the molten condition or when dissolved in water, therefore, it becomes a good conductor.

The case of magnesium ($N=12$) and oxygen ($N=8$) is similar except that two electrons are transferred from the magnesium to the oxygen atom. The resulting ions have their electrons arranged exactly like those of the neon atoms and the ions of sodium and fluorine. Therefore, the crystalline form of magnesium oxide and sodium fluoride should be identical, and this prediction of the theory has been confirmed experimentally by Dr. A. W. Hull by the X-ray method. Because of the much greater forces acting between the ions as a result of the double charges, the stability of the magnesium oxide is much higher than that of the sodium fluoride. This is manifested by the high melting point, low conductivity, low solubility, and hardness of magnesium oxide.

Phosphorus ($N=15$) and sulphur ($N=16$) have, respectively, 5 and 6 electrons more than neon, and are thus capable of giving up these numbers of electrons. If these elements are brought into contact with an excess of fluorine (which because of its proximity to neon has a particularly strong tendency to take electrons) all the extra electrons pass to fluorine atoms. Thus a sulphur atom will supply electrons to 6 fluorine atoms and will form the compound SF_6 . The force acting between the fluorine ions and the central sulphur ion is still electrostatic in nature it must be nearly 6 times greater than the force between sodium and fluorine ions. Furthermore, the 6 fluorine ions would surround the sulphur ion so that there would be little stray field of force. Therefore, we should not expect sulphur fluoride to be salt-like in character but to consist of very stable molecules having weak external fields of force and, therefore, readily existing in the form of a gas. As a matter of fact, this extraordinary substance has these properties developed to such a degree that it is an *odourless and tasteless* gas with a boiling point of -62 deg. Phosphorus pentafluoride, as it would be expected from its less symmetrical structure, is a gas having greater chemical activity.

The fluosilicate ion SiF_6^- has a structure exactly like that of the sulphur fluoride molecule, since the number and arrangement of the electrons are the same. This is clear if we consider that the atomic number of silicon is 14 while that of sulphur is 16. Thus if we should replace the nucleus of the sulphur atom in a molecule of sulphur fluoride by the nucleus of a silicon atom, without disturbing any of the surrounding electrons, we would have removed two positive charges and would obtain a negative ion with two negative charges of the formula SiF_6^- . In the presence of potassium ions we would then have the familiar salt potassium fluosilicate. The theory is thus capable of explaining typical complex salts. In fact, it is applicable to the whole field of inorganic compounds covered by the work of Werner, and helps to simplify the theory of such compounds. There is no time, however, to go into this subject.

The simple theory of atomic structure which we have discussed thus far explains perfectly what has usually been called "the maximum positive and negative valence." The maximum positive valence represents the number of electrons which the atom possesses in excess of the number needed to form one of the particularly stable configurations of electrons. On the other hand, the maximum negative valence is the number of electrons

which the atom must take up in order to reach one of these stable configurations.

For example, magnesium has a positive valence of two, since its atomic number is 12, while that of neon is 10. Sulphur has a positive valence of 6, since it has 6 electrons more than neon; but it has a negative valence of two because it must take up more electrons before it can assume a form like that of the argon atom.

It is clear, however, that this theory of valence is not yet complete. It is not applicable to those cases where we have usually taken valences of 4 for sulphur, or 3 and 5 for chlorine, &c. But more especially it does not explain the structure of organic compounds and such substances as H_2 , Cl_2 , O_2 , N_2H_4 , PCl_3 , &c. (The theories of Kossel, Lacomblé, Teudt, &c., which have recently been proposed in Germany, have not advanced beyond this point and are therefore very unsatisfactory as a general theory of valence.)

J. J. Thomson, Stark, Bohr, and others had suggested that a pair of electrons held in common by two adjacent atoms may function in some cases as chemical bonds between the atoms, but this idea had not been combined with the conception of the stable groups of electrons or octets. G. N. Lewis, in an important paper in 1916, advanced the idea that the stable configurations of electrons in atom could share *pairs* of electrons with each other, and he identified these pairs of electrons with the chemical bond of organic chemistry. This work of Lewis has been the basis and the inspiration of my work on valence and atomic structure.

As a result of the sharing of electrons between octets, the number of octets that can be formed from a given number of electrons is increased. For example, two fluorine atoms, each having seven electrons in its outside shell, would not be able to form octets at all except by sharing electrons. By sharing a single pair of electrons, however, two octets holding a pair in common required only 14 electrons. This is clear if we consider two cubes with electrons at each of the eight corners. When the cubes are placed so that an edge of one is in contact with an edge of the other a single pair of electrons at the ends of the common edge will take the place of four electrons in the original cubes. For each pair of electrons held in common between two octets there is a decrease of two in the total number of electrons needed to form the octets.

Let e represent the number of electrons in the outside shell of the atoms that combine to form a molecule. Let n be the number of octets that are formed from these e electrons, and let p be the number of pairs of electrons which the octets share with one another. Since every pair of electrons thus shared reduces by two the number of electrons required to form the molecules it follows that $e = 8n - 2p$ or $p = \frac{1}{2}(8n - e)$.

This simple equation tells us in each case how many pairs of electrons or chemical bonds must exist in any given molecule *between the octets formed*. Hydrogen nuclei, however, may attach themselves to pairs of electrons in the octets which are not already shared. For example, in the formation of hydrogen fluoride from a hydrogen atom and a fluorine atom there are 8 electrons in the shells ($e=8$). We place $n=1$ in the above equation and find $p=0$. In other words, the

fluorine atoms do not share electrons with each other. The hydrogen nucleus having given up its electron to the fluorine atoms attaches itself to one of the pairs of electrons of the fluorine octet, and thus forms a molecule having a relatively weak external field of force. As a result, hydrogen fluoride is a liquid of low boiling point instead of being salt-like in character.

The equation given above is applicable to all types of compounds. For example, if we apply it to substances such as sodium fluoride, sulphur fluoride, or potassium fluosilicate, which were previously considered, we find in each case $p=0$. In other words, there are no pairs of electrons holding the atoms of these compounds together. On the other hand, if we consider the compound N_2H_4 , we find $p=1$. Since there are only two octets, the pair of electrons must be between the two nitrogen atoms while the hydrogen nuclei attach themselves to pairs of electrons of the nitrogen octet. It can be readily shown that this simple theory is in fact identical with the accepted valence theory of organic chemistry and leads to the same structural formulas as the ordinary theory in all those cases where we can take the valence of nitrogen to be 3, oxygen and sulphur 2, chlorine and hydrogen 1. In other cases, such as those where quinquivalent nitrogen has been assumed, the new theory gives results different from the old, but in each case in better agreement with the facts.

The theory indicates a series of new relationships between certain types of substances which I have termed *isosteric* substances. For example, it indicates that the molecules of carbon dioxide and nitrous dioxide and nitrous oxide should have nearly identical structures and this is borne out by the extraordinary similarity in the physical properties of these gases. Nitrogen and carbon monoxide constitute another pair of gases which are similarly related. The same theory also points out a number of previously unsuspected cases of similarity of crystalline form (isomorphism.)

It is clear that in the past the term valence has been used to cover what we may now recognise as three different types of valence, as follows:—

1. Positive valence: the number of electrons an atom can give up.
2. Negative valence: the number of electrons an atom can take up.
3. Covalence: the number of pairs of electrons which an atom can share with its neighbours.

It is recommended that only for valences of the covalence type should definite bonds be indicated in chemical formulas. One of the particular advantages of the present theory is that it becomes easy to distinguish between covalence and the other types and thus to predict with certainty in what way electrolytic dissociation will occur, if at all.

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RUSSIA'S CONTRIBUTION TO SCIENCE.*

By ALEXANDER PETRUNKEVITCH, Ph.D.

WHILE Russian literature, Russian music, Russian art, and Russian dance are fairly well known to the American people, few realise the extent of Russia's contribution to science. This is quite pardonable considering the lack of knowledge on the part of the broad public of the ever growing achievements of exact science in all its branches, regardless of nationality, and taking into account also the difficulty of even casual acquaintance with subjects which require special training. To this must be added that a great deal of the work published by Russian scientists has been written in foreign languages, mostly in German and French periodical publications, while Russian publications are few and of these only one or two are known to foreigners.

In Russia itself education in general and science in particular has been for a long time unpopular, has been limited to a comparatively small circle of people and has even at the present time not yet penetrated into the broader masses. Purely clerical knowledge of the Tsarist Russia gave way to military training and to such education as was necessary for service in the bureaucratic institutions created by Peter the Great. Later humanistic studies and law became the standard of good education and dominated Russian society and Russian thought until comparatively recently. Medicine of course was early recognised as necessary knowledge, yet the people regarded it in the light of special knowledge rather detrimental to broad education. Applied science, such as engineering, was for a long time looked upon in the same way with the additional stigma of mistrust. Pure science has been looked upon rather as a hobby for men with sufficient means, dangerous in as far as it inclined to produce a critical attitude toward religion and the established order of things, undesirable inasmuch as it did not open any other field for activity than an academic career, and insufficient as a general basis for broad education. Yet in the second half of the past century pure science came into its own, conquered the opposition of society and furnished many a name looked upon with esteem and even admiration in Russia and far beyond its political frontiers.

To say that Russia might have produced a great deal more in the field of science than it actually has produced, had the development of the country been allowed to proceed normally, is not a mere figure of speech or an excuse, an attempt as it were to find extenuating circumstances for natural shortcomings. In a country where the word "constitution" was struck by the censor even from the pages of learned investigations, where the chief duty of the Secretary of Education was to devise means to prevent the spreading of knowledge, creative work in science was more than simply hampered, it was often physically impossible. Yet a glance at a list of works published by Russian scientists will show the productivity and many-sidedness of the Russian genius. There is scarcely a field of science in which Russians have not done some creditable work, increased the

* From the *Transactions of the Connecticut Academy of Arts and Sciences*, June, 1920.

store of our knowledge, cleared up some intricate problem or opened new chapters, and set forth new questions.

And all this had to be done in the face of great difficulties of which western institutions have no idea. There was always a lack of funds and a lack of men, a lack of institutions and a lack young men to be trained for such institutions. The educational system was borrowed from Germany, its negative qualities were intensified while the most important positive qualities were partially or completely suppressed. The Russian national character was not taken into account by that system foreign to its spirit which was put as it were into a straight-jacket and had its wings clipped by two most efficient tools in the hands of autocracy—censorship and espionage. Used persistently with only occasional short intermissions, during more than one century, and embracing all phases of national and private life, being constantly present in all university recitation halls, laboratories, and even private offices, censorship and espionage ruined the relationship between teacher and pupil, affected the character of the institutions, and prevented the normal development of many a promising youth.

To understand the ruinous influence of espionage and censorship on national character and the productive genius of the people one must have grown up and gone through the schools in Russia. The offices of inspector and his aids in every secondary school were especially created to control not only the behaviour of pupils in the school, but their life outside of school walls. The teachers themselves were subject to this supervision and dreaded the never-closing Argus eye of the inspector. The duties imposed on them, the general atmosphere of life amidst poverty, suspicion, bribery, and Simonism, prevented the teachers of secondary schools from doing original work of any character. Such work, not uncommon in Germany, is of the rarest occurrence in Russia, and only teachers of quite remarkable ability managed to step out of the high-school routine and drudgery into the broader field of an academic career. The Russian "Gymnasia," the Russian "Realnoje Uchilishtche" were patterned after the German "Gymnasium" and "Realschule," but the spirit of reactionary orthodox Russian autocracy was added to the German worship of authority and discipline of mind and will, and coupled with corruption, pervaded everything and corrupted and perverted the growing mind. It is a wonder under the circumstances that the mind, the spirit of Russian youth was not completely crushed in its instinctive upward struggling for light and knowledge and free expression of self.

The entrance into the sacred precincts of the highest education was purposely made difficult to prevent an undesirable growth of knowledge in wider circles. Only pupils who had studied in a gymnasium and had therefore had seven years of Latin and six years of Greek, and who passed the examinations at the end of their studies extending altogether over eight years, had the right to study at a university. Yet it may not be quite out of place to mention here that a boy entering the university in Russia knows no more of mathematics than a high-school boy in America and knows even less of physics and chemistry, while biology was not on the programme of studies at all.

One was allowed to postpone military training until after the studies at the university had been finished, and in the cases of men preparing for an academic career military training was altogether waived. This exemption applied both to those who became teachers at schools and professors at universities. But the requirements for professorial positions were so high, as we shall see later, that the exemption from military training was in no sense an inducement.

On entering the university the student had to follow a prescribed course of studies through all four years, but could and was expected to take also other courses, provided they did not coincide with the obligatory ones. A course in theology, *i.e.*, in the dogma of the Russian orthodox church, was compulsory for every student in the first year of his studies. Compared with the American colleges the work at the Russian universities is much heavier, the number of hours is considerably greater, and the number of subjects required cover a much wider range. It was customary to work Saturday afternoon and some classes were given even on Sunday mornings, as for example entomology at the University of Moscow at the time that I was studying there. To give an idea of the scope of studies required at a Russian university from a student in natural sciences preparing for an academic degree, I shall simply enumerate the subjects which I myself had to study in Moscow: Physics (four hours per week during two years); inorganic chemistry (first year); qualitative analysis and quantitative analysis (second year); organic chemistry (third year); physical geography (one year); geology and paleontology (one year); mineralogy and crystallography (one year); meteorology (one year); human anatomy (one year); physiology (one year); histology and embryology (one year); introduction to zoology (one year); invertebrate zoology (one year); vertebrate zoology (one year); entomology (one year); botany (three years) including general morphology, anatomy, physiology, and systematics; and theology (one year). In the first and second year the spare hours were given to economics and principles of law. During the last term of the fourth year a thesis has to be written on a subject assigned by the professor, consisting of a review of work done by other workers, and some original investigation. After a six-hour written examination on some subject in the department of study chosen by the student, and after oral examinations in all subjects studied during the third and fourth year, those studied during the first and second year having been disposed of previously, the student receives a university diploma conferring on him the degree of *Candidat rerum naturalium*, which as may readily be seen is a much higher degree than either the corresponding degree of the German universities, or the B.A. of American colleges. It will also be seen from the foregoing that the training of a Russian student at the end of his studies is in every respect broader and covers a much wider range of subjects than either that of an American or a German student.

Students with exceptionally high standing, who desire to follow an academic career, are allowed to continue their studies at the university after they have received their degree. They have no more lectures to attend, but receive a general outline of reading and work to be done as a prepara-

tion for an examination which will give them the right to present a thesis for the degree of Magister in the subject which they have chosen, *i.e.*, Magister of Chemistry, Magister of Botany, &c. This examination may under no circumstances take place sooner than two years after the examination for the degree of Candidat. It is one of the stiffest examinations imaginable and the amount of reading required is simply appalling. To give even an approximate idea of the ground which has to be covered by the candidate during these two years, I shall only mention that in my own case the books recommended to me by my professor occupied more than a five foot shelf and contained such works as Bronn's *Classen und Ordnungen* and similar works, all of which were supposed to be used not as reference books but as text books and the detailed information contained in them to be kept in one's memory ready to be drawn upon at a moment's notice. It has happened time and again that candidates were flunked because they were unable to produce from memory facts which the examining professor himself knew only because he was recently engaged in research on the subject.

After the successful passing of this examination the candidate receives the title of *Magistrant* and is admitted to lecturing and laboratory work in the capacity of a *privat-dozent*, a title also borrowed from the Germans. At the same time he must present his thesis for public discussion before he receives the degree of Magister. This dissertation has to be the result of an original investigation and to cover the ground thoroughly. It has to review the literature of the subject as far back as possible, in some cases going actually back to Aristotle. The public defence is no sinecure, for the officially appointed opponents take especial pleasure in tearing the arguments and evidence to pieces and in pointing out the slightest flaw in the treatment of the problem.

If the degree has been awarded the holder of it may now be appointed "extraordinary professor." Within not less than two years nor more than ten he has to present a second dissertation for the highest degree attainable, that of Doctor, not Doctor of Philosophy as in Germany or America, but Doctor of the special science which he has chosen. The degree of Doctor of Philosophy in the American sense of the term does not exist in Russia, and whenever a professor is in possession of a Russian degree of Doctor of Philosophy, that means that he is a specialist in philosophy.

It will be seen that it is utterly impossible for a Russian to possess more than one degree of Doctor, unless it be an honorary degree which is scarcely ever given. The only exception is the degree of Doctor of Medicine, which strange to relate, does not need to be preceded by a Magister degree, is often given for some quite unimportant and small piece of work, and comes nearest to the German M.D., especially since it has to follow upon an examination without which practice is not allowed. But the training of the medical student in Russia is also vastly broader than in the United States, and the scope of knowledge possessed by the average Russian practicing physician has often been a subject of admiration to foreigners.

But the amount of work required of those who prepare for an academic career has also its negative side. Memory is easily overburdened with unnecessary details, much valuable time is lost in

gathering the knowledge required for the examinations, and perhaps still more in reading and reviewing the work done by others, which in the majority of cases has long ago lost all scientific value and in many cases might have been better forgotten altogether. What with the academic duties of lecturing, laboratory work, committees, &c., the creative ability is easily stunted, and unfortunately it is not an uncommon occurrence that the dissertation for the Doctor's degree is the last original work of the overburdened professor. Only the more talented and more pertinacious hold out under the strain and continue as investigators.

And all the time the outside life invades the peaceful premises of the university and asserts itself in the most uncompromising manner. Neither the Russian student nor the Russian professor can avoid its influence. Censorship and espionage are more developed and stricter in the university than elsewhere, and it seems that in this respect the renowned Bolshevik reformers and heralds of educational freedom for the poorest citizen have far outdone the old Tsarist advocates of the muzzle and whip. But censorship and espionage notwithstanding, the professor and student alike have to possess a distinct reputation as belonging either to the progressive or to the reactionary political group, and no liberal minded assistant may continue indefinitely to assist a reactionary professor. He has ultimately either to ally himself definitely with the reactionary elements or to resign. As a general rule we may say that the best work was done by progressive professors, although some very reactionary men have contributed creditable work in their particular field of learning. But real expression of political views was not possible except for a short period in the sixties and again after the revolution of 1905, and even then it had to be sufficiently guarded.

The first scientific institution created in Russia was the Imperial Academy of Sciences, and its foundation was due to the genius of Peter the Great, who conceived the idea and had conferences regarding its execution with Heinrich Fick as early as 1718. Dr. Blumenrost prepared a project which was approved by Peter in 1724 and according to which the Academy should be not only a research, but also an educational institution. Peter died in 1725 and it was his widow Catherine the First who ordered the opening of the Academy on November 12, 1725, and fixed its yearly budget at 24012.00 Roubles. Foreigners, mostly Germans, were invited as professors. About the year 1727 there were seventeen of these, including such men as Hermann and Goldbach in mathematics, Nicholas Bernulli in mechanics, Buerger in chemistry, Biefinger in physics, Duvernoie in anatomy and zoology, Leonhard Euler in mathematics, &c. The eight students who had to study with these professors were all Germans, all imported for the purpose from Germany. By the year 1742 there were as many as twelve students. In 1747 the Academy was divided into two sections—the *Academy* proper, and the *University*. The internal organisation of the Academy was changed in 1803 and again in 1836 and in 1841, when it was sub-divided into three sections. The *Memoirs of the Academy* are so well-known and contain so many important articles in all branches

of science that we do not need to consider them here further.

The Academic University died a natural death through lack of students, and the first Russian university must be considered to be the University of Moscow, which was opened in 1754, and had as many as one hundred students in 1758. In 1804 a constitution was adopted, framed on German model by W. N. Karasin. This constitution recognised the autonomy of the university and was extended to the newly founded universities in St. Petersburg, Kazan, Kharkov, Vilno, and Dorpat. In 1830 the University of Vilno was abolished and that of Kiev opened. In 1835, however, the constitution was modified. The number of students was limited, and the Government appointed special curators to control university affairs. The last traces of academic freedom were obliterated in 1849, when the new constitution framed by Prince Shirinsky-Shikhmatoff was introduced into all universities. All executive officers and all professors were from now on appointed and not elected, and "harmful" sciences, such as constitutional law, were forbidden. The liberating and progressive movement at the beginning of the sixties brought with it a change in the universities also. A new constitution prepared by Golovin restored academic freedom, but only for a short period. In 1866 Count Dmitri Tolstoy was appointed Secretary of Public Instruction and began immediately to interfere with the work of the universities by means of special decrees. A constitution prepared in accordance with his suggestions was introduced in 1884, when Delyanoff was Secretary, and from now on until the revolution of 1905 the universities were entirely under the strictest control of the government. A short breathing space after the revolution, then oppression worse than before; then again a sudden wonderful efflorescence of freedom in 1917 and now almost complete ruin under the Bolsheviks!

Such is the sad history of the Russian universities which played such a glorious rôle in developing Russian youth, in combating reaction based on ignorance and avarice, and in contributing through the patient work of their professors to the store of human knowledge. Only a century of existence, a century of martyrdom! During that time many thousands of students were never allowed to finish their education, some banished to Siberia, others imprisoned, many killed. And during that time many professors were removed from office, banished, censured, imprisoned, broken in spirit. And in the aftermath of the revolution some of the best among them have died of starvation others have been executed and all execrated as enemies of the proletariat.

Yet even in the darkest hours and years of reaction the universities continued their work in science. Every university has its own publications in the shape of transactions or proceedings, or of similar publications of societies organised by the universities. Especially well known are the publications of the St. Petersburg Mineralogical Society, of the St. Petersburg Society of Naturalists, of the Moscow Society of Naturalists and of the Moscow Friends of Natural Sciences, Anthropology, and Ethnography. But, other publications, such as the Proceedings of the Society of Naturalists of Kazan, founded in

1869, and those of the corresponding society of Kiev, also founded in 1869, and of Kharkov contain many valuable and important articles. Men who studied at universities but who were forced by circumstances to live in cities which had no university or other higher educational institution, founded small scientific societies, little local museums, as the Society of Naturalists in Ecaterinburg, which publishes its own proceedings, another similar society in Saratov, again one in Tiflis, and anthropological and ethnographical museum in Twer, and so on. The foreigners can have scarcely any idea as to how much all these publications contain of material referring to local fauna, local flora, local ethnography, &c. The various Governmental Departments have been also publishing many important contributions to our knowledge both in pure and applied sciences, geological, mineralogical, entomological, investigations. Reviews of Russian contributions to the various branches of science have been printed from time to time, such as Anatoli Bogdanoff's "Materials for the History of Pure and Applied Zoology and of Allied Branches of Knowledge in Russia," 1850; Sabaneeff's "List of books and papers on hunting and nature study," 1883; G. A. Kojewnikoff's "Reports about Russian Zoological Literature," 1893, &c., but the special work which was in preparation when the revolution disrupted all university work in Russia, and which was to embrace all branches of science in a way similar to the volume dealing with humanistic sciences, has been interrupted by the upheaval and may have been lost.

(To be continued).

EDITORIAL.

WITH a view to increasing the usefulness of the CHEMICAL NEWS, it has been decided to introduce in the near future a new feature in the method of publication. It was the aim of the late Sir William Crookes, that the CHEMICAL NEWS should be the medium for the publication of original thought among Chemists and Physicists, and in its columns most of the discoveries of the past fifty years have appeared; in some cases the CHEMICAL NEWS was the first organ of publication.

The present Editor desires that the Journal shall maintain its useful character, and is anxious to meet as far as possible the many suggestions that have been made to this end.

Recently numerous original communications have been received, but lack of space and difficulties in printing have caused delay in publication; these difficulties are likely to increase rather than diminish.

It has therefore been decided to arrange a weekly "Editorial Notice", to announce, and if possible give a brief summary of, any papers received during the week, but of which, for the reasons stated, publication may have to be deferred.

The Editor therefore suggests to authors that a short summary should accompany original com-

munications, so that an announcement can appear immediately. Such announcements must be very brief, and should at most occupy but a few lines, giving only such details as are necessary for immediate publication.

The Editor would be grateful for any further suggestions that would help to make the **CHEMICAL NEWS** of greater value to the profession generally and to maintain its character as a means of publication of original thought in Chemistry and Physics.

NOTICES.

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NOTICE.

OWING to the greatly increased cost of printing and paper, and the advance in the postal rates, we have been compelled to raise the price of the **CHEMICAL NEWS** from 4d. to 6d. (by post 7d.). The new subscription rates are as follows:—

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3145.

EDITORIAL.

THE following papers have been received for publication, and will be inserted as space permits:—

"Fruit of the Japanese Barberry." By O'Neal Mason. (From Cornell College, Iowa, U.S.A.).

"A Chemical Examination of the Berries dealing with the Sugars, Ash Oils, and the Proteins." (From Cornell College, Iowa, U.S.A.).

"A Study of Dolomites." A history of the life of Deodat Dolomieu and the discovery of Dolomite, with a study of a number of specimens from Ward's Natural Science Establishment, Rochester, New York. (From Cornell College, Iowa, U.S.A.).

"The Spectrochemistry of the Mono-, Di-, and Tri-Azenes." By Gervaise Le Bas. A study of the molecular refraction of these compounds and discussion of some new facts resulting.

"Isotopism." By J. Frederick Corrigan. The paper deals with the theory of isotopes, and traces the subject from the late Sir William Crookes's theory of Meta-elements to the present time. Received July 15, 1920.

"Isomerism, Tautomerism, and Pseudomerism of Organic Compounds and their relation." By Ingo W. D. Hackh, College of Phys. and Surg., San Francisco, California. The purpose of this paper is the formulation of a system and classification of isomeric organic compounds to enable a clear definition to be formed of the terms, based upon their structural differences. Received June 2, 1920.

Our attention has been called to an error that occurred in our issue of September 19th last. An article on the "Activation of Carbon," by N. K. Chaney, was ascribed to the *Canadian Journal* instead of to the American Electrochemical Society. We are glad to correct the mistake.

WHEN IS POISON NOT A POISON?*

By JOHN URI KLOYD.

A REPLY to the above question might be: When, for any reason, a substance is harmless in action, immediate or remote, be it applied externally or taken internally. In other words, it is *not then* a poison.

This leads to the question: "Can a substance be considered as a poison at one time and innocuous at another?" To this one might make several replies, as the problem is viewed from its several side-angles.

For example, sulphuric acid, in concentrated form, applied to the skin or taken internally, will at once disintegrate flesh. Its action is then that of a corrosive agent, its destructive influence rest-

ing directly upon avidity for water and its power of abstracting water from liquids and even from tissue, to the tissue's complete destruction. It thus, under these conditions, becomes a corrosive poison.

As an example, one might state that white sugar is a carbohydrate, composed of carbon and the elements of water in the proportion to theoretically produced water. Place a lump of white sugar on a plate and then pour upon it a little concentrated sulphuric acid. Immediately it turns yellow, then black, owing to the liberation of carbon (charcoal) by the abstraction of its companion oxygen and hydrogen, which the acid takes, to the destruction of the sugar.

Dilute the same amount of sulphuric acid with water, to pleasant acidity, and it no longer destroys tissue on contact therewith, nor is it immediately harmful to the stomach. The sugar dissolves in it, colourless, when it is thus diluted. Indeed, as an acidulated drink (circus lemonade), much diluted and flavoured with lemon oil, it has been used, without immediate corrosive effect or injury, as a substitute for lemonade. This practice, however, is now wisely forbidden.

To sum up, in one form, sulphuric acid is destructive to living tissue; in another form (dilute), it acts differently. The amount that, concentrated, would disintegrate tissue if applied locally, is, when diluted, harmless.

Take next arsenic. With the normal human being, arsenic, in comparatively small doses, is death-dealing. But with some persons, artificially made immune, a dose that poisons others is harmless. Arsenic eaters come within the scope of habit-forming drug addicts. The habit-formed principle applies likewise to morphine and similar drugs. Be the arsenic or morphine dilute or concentrated, a toxic amount to the normal man acts as a poison. Be it for example, six grains of morphine, in substance, or six grains dissolved in an ounce of water, the same exerts its poisonous influence, providing the whole amount be taken at a single dose. Indeed, dilution may even increase its activity.

Be it said that, although arsenic, morphine, and such as these act as poisons upon the normal man, an individual may, as above stated, accustom his system to the drug, so that enormous doses may be taken without apparent injury. In this no comparison can be made with the cited action of sulphuric acid, of which a drop on the skin of any man will bite its way to the tissue beneath, but yet can with impunity be swallowed when diluted with water.

We may likewise pass to other material that exercise special influences, but where, so far as we know, artificial habit-forming methods have no part. *Rhus toxicodendron* both excretes a substance and carries a volatile something that produces violent toxic action on some persons, while to others it is as harmless as bedewed grass. A waft of air over the dew-covered vine may close the eyes of a strong man exposed to its painful influence, may cover his body with a painful eruption, may drive him to seek his physician's aid.† Another man or a fragile one comes next

* Definition—Poison: "Any substance applied to the body ingested, or developed within the body, which causes or may cause disease."—DORLAND.

† The remedies offered as "poison ivy" are legion. This writer believes that the action is often due to the body-bred toxins. The chain of systemic reactions that the body-bred toxins may be likened to the Biblical "third and fourth generations."

and with impunity, with bare hands, pulls the vine from its fastenings. The eyes of the first man may be closed by the attenuated "poison", imperceptibly attenuated by the gentle breeze, beyond the chemist's art to identify, while the other person, bespread with its juice, has not even a pimple on his hand. Thus, "poison ivy" is, or is not, a poison, as the individual is or is not susceptible to its influence.

As an illustration, the writer each year has laboratory use for many thousand pounds of rhus toxicodendron (poison ivy). The green leaves, when in their prime, are gathered by collectors, who in midsummer, with bare hands and arms, strip the vines, crush the green leaves into sacks, and deliver the product with impunity. No immediate, or after-effect, is noticeable. One young lady of the laboratory force is so sensitive to the action of the drug as to respond to the emanations, although she be in a distant part of the establishment. To bottle and label "Rhus", or otherwise handle a preparation, means to her typical rhus poisoning. Consequently, at such time, she has a vacation, not being allowed within the establishment.

Once we knew a man to be vaccinated with a virus-crust, that used in equal amount on others, produced no untoward action. And yet that man came near losing his arm. It is evident that not the virus, but the man, or some undetermined local cause connected with his case, was then at fault. The *virus* was the actual disturber. Let us not overlook that in such cases as these local conditions, such as the syringe needle or skin uncleanness, may be at fault, not the virus.

Physicians may recall the use of a hypodermic syringe from season to season, with no complaint. Then, in the course of ordinary injections, a patient is "poisoned" by the same dose of the same medicine previously employed, and injected with the same syringe needle. The question arises, what caused this exceptional action? Blame is likely to be attached to the virus, regardless of its innocence.

One might fairly imply that either in this one case the syringe needle was infected, or that a shred of foreign matter was injected, or that this one patient was exceptionally sensitive to the remedy employed. Vaccines are not in our sphere; we make no claim to capacity to speak as an expert in this field. But yet letters from patrons citing exceptional experiences in these directions lead us to accept that where one person, and only one, experiences such exceptional results with a preparation where hundreds of others find no untoward effect, the cause may be accepted as local or systemic, its exceptional action lying outside the preparation used. Such as this is a problem for serious study.

Full well it is known that tobacco is destructive the life of most insects, and yet there are worms thrive on the green leaf, as well as insects breed the dried drug, and delight in the cigars. To the one, green tobacco, to the other, tobacco is a food. And yet, this tobacco made "deathly sick", as frightened people testify, when a film of collodion containing a drop of nicotine was applied to the nail, on the first joint of his finger. Moments alarming results followed. The nail was once washed off

with chloroform, ammonia to the nostrils and stimulants internally being promptly administered. And yet, without any untoward influence, thousands of employees breathe with impunity the close air of tobacco warehouses, cigar factories, and constantly handle strong nicotine tobacco leaf.

Capsicum, in substance, is heroic, as all who have experienced its direct action will testify. But yet a beetle (undetermined, so far as we know), feeds on powdered capsicum, and burrows in its depths. To that insect capsicum is a choice food, and to the Mexican, in excessive amounts, it is but a pleasant condiment.

The plant known as sanguinaria (blood root) contains large amounts of energetic alkaloids that vomit man, when taken even in small doses. And yet a single mole exterminated a bed in which this essayist took much pride. At least, by circumstantial evidence, the mole got the blame for the offence.

In like manner, biologists are aware that heroic poisons fail to act with some animals, while substances "not a poison" are destructive to others.

"Chambers" is authority for the assertion that natives of Africa drive hogs through serpent-infested sections, the hog not being susceptible to the virulence of that viper. It is stated that the beast presents its cheek to the serpent, then grasps the reptile in its mouth. Tradition has it that the hog is likewise immune to arsenic. Country people have a tradition that a full pail of milk from a newly-calved cow will kill a hog. The father of this essayist doubted the statement and fed a valuable hog a full portion of the first milking. The hog died that night. Seemingly, the experiment succeeded. And yet the cheese made of the first milking of the "nannie goat" commands exceptional value in Smyrna.

The miasmatic fog that catches one person may fail to affect neighbours equally exposed. A plague may sweep away a multitude and yet miss an individual member of that multitude.

Thus we find the term *poison*, whatever the dictionary definition may be, carries undercurrents of opportunities for questionings, as well as investigations, that make the answer to the question, "When is a poison not a poison?" more of a problem than a cursory glance would indicate.

And yet, since, as a rule, such peculiarities as these are exceptional, a cause for each exception unquestionably always exists. The *reason* therefore, in obscured conditions, is an opportunity for science research, the facts having, as a rule, been incontrovertibly established by empirical record. The man of experimentation, opportunity, and thought has surely, here as elsewhere, accomplished his share in the chain of progress when he hands to his co-labourer a statement of fact based on balanced observation.—*Eclectic Medical Journal*, April, 1920.

IMPORTANCE OF THE JAVA SUGAR INDUSTRY.

JAVA is the third largest sugar-producing country in the world, ranking next to Cuba and British India. As the last consumes practically all that it produces, Java ranks next to Cuba in sugar exports, actual production being about half of the

Cuban output, and approximately three times the production of the Hawaiian Islands. Compared with the Hawaiian industry, where, it is understood, there are about fifty sugar centrals, Java has at present 186 producing mills.

It appears from a report by the United States Consul at Soerabaya that, on account of the density of population in Java, which is estimated now to be more than 30,000,000, the Government does not permit of large concessions of land, and will allow the use of any given tract of land for sugar production for only one year out of three, requiring that rice be planted for the other two years. This necessitates a rotation of crops in three-year periods, and continually reserves two-thirds of the available sugar land for the production of rice. This has been found to be a very wise provision, since, even under the present system, the consumption of rice is greater than the production in Java in normal years, so that the country is somewhat dependent on the near-by rice-producing countries for imports of the staple food supply. During last year there was, in fact, considerable discussion looking toward the further restriction by Government of sugar cultivation, in order that the local rice production might be increased. This proposal was eventually abandoned, however, in view of the importance and value of the sugar crop at the present time of great world demand and consequent high prices.

The sugar-mills are for the most part large modern plants, although some of the labour-saving devices in common use in many other countries are not used owing to cheap and plentiful labour. There is now, however, a growing interest in labour-saving appliances and machinery, due to the increased cost of labour and a certain amount of labour trouble which seems to be prevalent to-day in Java as well as other parts of the world. Java sugar-growers are now, for the first time, coming to a realisation of their rather precarious situation in depending so completely on unskilled labour.

It would appear that the time for the introduction of labour-saving machinery is rapidly approaching, and careful and systematic efforts by manufacturers in this direction should bring results during the next few years. Most of the estates are supplied with light railways, operated with small, light wagons, but many still rely largely on bullock-carts for bringing the cane to the mills and native labour in handling it. Many estates use small wagons on the light railways, either pushed by hand or drawn by bullocks, while only a few have locomotive equipment.

The transportation of cane is especially difficult in Java, because of the fact, above mentioned, that planted areas are in small plots interspersed with plots of rice paddy, so that a plantation of 2000 acres of cane is compelled to extend its transportation system over territory of three or four times that amount of land. Figuratively speaking, a plantation of four square miles of cane, where the longest haul would be about a mile if the mill were placed in the centre of a compact tract of that size, would require a long haul of more than two miles, if only a third or fourth of the land is in cane. Actually the difference is, in many cases, considerably greater than in the above hypothetical case, since the plots are not arranged with mathematical pre-

cision. A certain plantation, for example, of approximately 4000 acres under cultivation, must haul the cane about eight miles from some of its more distant fields. As the plots are changed from year to year, much of the light railway must be portable.—*Journal Royal Society of Arts*, July 9, 1920.

RUSSIA'S CONTRIBUTION TO SCIENCE.*

By ALEXANDER PETRUNKEVITCH, Ph.D.

(Continued from p. 35).

THE physical conditions of the country, the climate, the historical development, the political oppression, the economic backwardness, the general stagnation and hopelessness of life have moulded the Russian national character to a form differing from that of other nationalities. And as the Frenchman is different from the Englishman not in language and nationality alone, but in all qualities of mind as well, so the national character may be traced broadly speaking, not only in the sphere of politics, trade, or business, but also in other branches of mental activity. If the average quality of the German scientist is heavy thoroughness, that of the Frenchman clearness and lucidity of thought combined with an impulse to treat science as art, that of the British extraordinary positivity, and that of the American an ability to combine specialisation with mass production, then the distinctive character of the Russian may be seen in the restlessness of his spirit and the striving to embrace a wide field of knowledge, to find answers to questions which are ever present in his thoughts and which once raised may not be lightly put aside, but must be settled the one way or the other, if only for the satisfaction of his own soul.

These qualities have been manifested already by the father of Russian science, Michael Vassilievitch Lomonosoff, who came of peasant stock and gradually rose to the distinction of being the foremost man of science and letters in Russia. He was born in 1711 in a small village of the Government of Archangel in the dreary north, far from any civilisation. He learned reading with the aid of books given him by some villagers who took interest in him and when 19 years old, in 1730, went to Moscow to study at the so-called Slav-Latin Academy. Here he spent five years, living in poverty and studying with grim determination amidst boys many years his juniors, who laughed at the big, ignorant fellow. A glimpse of this period may be gained from Lomonosoff's letter to Shuvaloff written in 1753. "With an allowance of three pennies (altyn) a day, I was not able to spend more than a penny for bread, a penny for kvas (a Russian beverage), and a penny for paper, footwear, and other necessities. Thus I lived during five years, yet I did not give up my studies." From Moscow Lomonosoff went to Germany, where he studied mathematics, physics, and philosophy with Wolff, chemistry and metallurgy with Henkel. He spent five years in Germany and returned to Russia in 1741. The following year Empress Elizabeth appointed him Adjunct in Physics to the Imperial Academy. In 1745 he was appointed Professor of Chemistry in

* From the *Transactions of the Connecticut Academy of Arts and Sciences*, June, 1920.

the Academic University the foundation of which was due mostly to his influence. There he created the first Russian Chemical Laboratory in 1748 and in 1756 was the first to explain what we now understand as oxidation by converting tin into stannic oxide, antedating the work of Lavoisier on a similar subject by 18 years. Lomonosoff was one of the pioneers in work on atmospheric electricity and shares with Franklin the honour of the discovery of the lightning rod. He made the suggestion that electricity is responsible for the aurora borealis. In astronomy he was the first to discover the presence of an atmosphere around the planet Venus. He elucidated the nature of amber as balsam of extinct vegetation. He taught that anthracite originated from peat. All this was done at a time when science was looked upon as almost of the Devil by the Russian Church, and in his paper about the planet Venus, Lomonosoff took therefore particular pains to explain that there is no contradiction between science and the Bible.

But the activity of Lomonosoff was not limited to natural sciences alone. He was a historian with two important works in this field to his credit. He was a philologist and wrote a book on "Rhetoric," a "Grammar," and "Rules of Russian Versification." He was an orator and a poet. He was a statesman and prepared a project concerning trade, industry, agriculture, and education and another project for the foundation of a university in Moscow, which he planned to open to students in 1755 and was unable to do so only because of the unexpected death of Empress Elizabeth. He died in 1765 at the age of 54 years in the fullness of his powers and at the height of his mental activity.

I take another example, that of the great composer Alexander Porphyrievitch Borodin. To Americans he is known only as the composer of "Prince Igor," but although he achieved greatness in music he was by education and profession a chemist, a professor of this science at the University of St. Petersburg. He worked chiefly with haloides and to his credit are no less than 21 papers in chemistry. He was the first to produce benzoyl fluoride. He lectured for ten years to women students of medicine. He was a fighter for education for women, and when he died, his former students placed a wreath on his monument with the inscription: "To the founder, defender, and guardian of the medical classes for women, to the friend of pupils—from women physicians of ten classes."

And how about Nicolai Petrovitch Wagner, the discoverer of pædogenesis in insects, who received two prizes for his zoological investigations, one of them from the Paris Academy, and who achieved no lesser fame and endeared himself to all Russian children by his incomparable "Tales of the Purring Puss"? not to mention his less known novel in two volumes printed in 1890 and entitled "The Dark Path." How about the writer and critic Danilevsky, who published in 1885 two volumes on "Darwinism" in which he collected all evidence that could be brought against Darwin's theories? How about Ilya Ilyitch Metchnikoff, who first achieved fame as zoologist, changing later to bacteriology and the study of immunity, and occupying an assistant directorship in the Institut Pasteur in Paris where he died quite recently?

Yet the beginning of scientific study and research as we have seen was made by foreigners whom Peter the Great marked out for the work and Catherine the First called to occupy the first chairs in the Imperial Academy while Catherine the Second followed their example. Some of them became in time loyal Russians, others at least enjoyed Russian hospitality and conditions which were evidently more favourable to work than professorial positions in their own countries. To that extent at least the great Swiss mathematician Euler; the great embryologist Karl Ernst Baer, known in Russia where he was born of German parents and where he spent almost all his life as Karl Maximovitch; the German anatomist and physiologist, the creator of the Theory of Epigenesis, Kaspar Friedrich Wolff, born in Berlin in 1733 and called to Russia by Catherine the Second in 1766 and resident in Russia until his death in St. Petersburg in 1794, have contributed to Russia's share in science, and to avoid mentioning them would be as unfair to their memory as to avoid the name of Louis Agassiz in speaking of America's contribution to science. They were favoured, they were happy in their work in Russia. They became identified with the Imperial Academy, they printed their papers in the Memoirs of that institution which they and others after them made great.

It is not my purpose to present in this short sketch of Russia's contribution to science an outline of work in all branches of natural sciences. Nor do I intend to give a list of all men and women who contributed to the world's treasury of knowledge, still less to give a list of books and papers written by Russian scientists. Such a list would fill several stately volumes. All I desire is to recall to the memory of those who have always admired Russia and of those who have lately lightly condoned the destruction of Russian universities by fanatics and adventurers under the pretext that Russian men of science serve not the proletariat but wealthy bourgeois alone, to recall to their memory the great service rendered by Russia. And for this purpose I shall dwell only on a few of the natural sciences and mention only the most important work done.

Uppermost in my mind is chemistry, that particular science for which lately the Germans more than other nationalities were admired. But Voskresensky, Zinin, Beketov, Butlerov, Beilstein, Mendeleeff, Menshutkin—what a cluster of names of which any country may justly be proud! Although Lomonosoff had been the first to teach chemistry and created the first chemical laboratory, the "Grandfather of Chemistry in Russia" is usually considered to be and is known under that endearing nickname Alexander Abramovitch Voskresensky, born in 1809 in the city of Torjok, in the Government of Tver. He was the teacher of Mendeleeff, who always spoke of him with reverence and admiration. His works were numerous and covered a wide field of research. He studied various reactions of sulphuric anhydride. But his chief work was in organic chemistry. He was the first to discover and describe the quinones, to elucidate the chemical structure of naphthalene, to find theobromine in chocolate. Nicolai Nicolaevitch Zinin, born in 1812 in the Caucasus and professor of chemistry in St. Petersburg from 1847 to his death in 1880, was so dis-

tinguished in organic chemistry, especially through his exhaustive investigations of benzene and its derivatives, that he was elected corresponding member of the academies of Paris and Berlin and of the London Chemical Society. He discovered naphthylamine (he called it naphthylidam), and described the preparation of amines from nitro compounds with the aid of hydrogen sulphide, a reaction of great importance in the production of modern aniline dyes, and still referred to as Zinin's reduction.

Nicolai Nicolaievitch Beketov, born in 1827, was one of the first theoretical chemists of his time, at a time when theoretical chemistry was not yet in vogue, and was particularly interested in the problem of chemical affinity which he made the subject of a number of articles.

Alexander Michailovitch Butlerov, born in 1828 and for many years professor in St. Petersburg, created a whole school of chemistry. He wrote a celebrated book entitled "Introduction to a Complete Mastery of Organic Chemistry" and dozens of special articles dealing with the derivation and structure especially of isomeric alcohols and hydrocarbons. It may be added that he was also an expert in bee-keeping and wrote a popular book on "The Bee: Its Life and the Rules for Rational Bee-Keeping," published in a cheap edition in 1871 and reprinted repeatedly. He was also interested in the occult questions of spiritism and achieved quite a fame in this field much to the dismay of his more materialistic colleagues.

Feodor Feodorovitch Beilstein, born in St. Petersburg in 1838, is sufficiently well known to foreigners as one of the most distinguished students of organic chemistry, who usually consider him to be a German because he wrote in German. Yet he lived all his life in Russia, where he was a professor, spoke Russian, and considered himself and was considered by his students a Russian. At least I remember him as such presiding over the examination in chemistry which I myself had to take in Moscow. The best known of his works is his "Handbuch der Organischen Chemie," the standard reference book on the subject, but he has published many special articles on aromatic compounds, on Russian petroleum, on molecular rearrangement, &c.

Nicolai Alexandrovitch Menshutkin, born in 1842, in St. Petersburg, a pupil of the Russian chemist N. N. Sokoloff and of the Germans Strecker, Wurtz, and Kolbe, is best known by his textbook of analytical chemistry, printed in 1871, reprinted since that time in many editions and translated into three foreign languages, but not less valuable is his "Lectures in Organic Chemistry" also published in many editions. His earlier work was on the synthesis and properties of carbamides, but later he was more interested in the question of the relation between isomeric alcohols and acids and esters, and received a prize for this work in 1878. Since the foundation of the Russian Chemical Society in 1868 Menshutkin was closely associated with it and was the editor of its journal. The British Association for the Advancement of Science elected him corresponding member. A complete list of his papers may be found in the second volume of the Biographical Dictionary of the University of St. Petersburg.

(To be continued.)

INCREASING DEMAND FOR GLASSWARE.

THE First Ordinary General Meeting of the shareholders of James Powell and Sons (Whitefriars), Limited, was held recently at the Hall of the Institute of Journalists, Tudor Street, Mr. WM. H. P. STEVENS (vice-chairman) presiding.

The SECRETARY (Mr. F. G. Orme, O.B.E., F.C.I.S.) read the notice convening the meeting and the auditors' report.

The CHAIRMAN, in presenting the report and accounts for the first six months' business, announced that a nett divisible profit of £3,493 had been made. The Company has purchased the freehold of fifty-eight acres at Wealdstone, Middlesex, upon part of which they are erecting an up-to-date Glass Factory, and they are proposing to form a Public Utility Society for the erection of comfortable houses to accommodate their workmen.

The business is being conducted upon a profit-sharing scheme by which all who are occupied in the undertaking receive a share in the profits.

Mr. A. MARRIOTT POWELL, the General Manager, then submitted the following statement:—Ladies and Gentlemen,—In the remarks that I have to make I desire, as briefly as possible, to put you in touch with the position of affairs as they appear to us who are responsible for the active management of the company's business to-day. To start with, I should like you to understand that, although the war is over, we are still to a considerable extent working under war-time conditions, particularly as regards the demands which are made upon us for glasses and goods which, before the war, we were seldom called upon to make. In pre-war days our factory was principally devoted to the manufacture of table-ware and other articles, wherein the actual glass itself was a comparatively small factor, and the bulk of the cost of each article consisted in the labour expended upon it. During the war we were called upon to make large and ever-increasing quantities of glass tube, which, though it was our finished product, was sold by weight, and became the raw material of the lamp-blowing section of the industry. The demand for tube and other glassware for scientific uses is almost incredible, and it is a fact that we have almost daily to refuse orders for lack, not only of the glass out of which to make it, but also of the space in which to make it. In our new works we shall have, I hope, ample space for the manufacture of glass, and for drawing it out into long lengths of tube.

Table Glass: Unable to Cope with Orders.

The demand for table glass, our principal pre-war product, seems to be steadily on the increase. We are totally unable to cope with the orders actually received from our old customers, and we are obliged to turn down all new enquiries, especially those for the wholesale and export trade. There is no doubt, therefore, that we shall find a very ready sale for some years to come of all the glass of every type that we shall be able to manufacture at our new works when we have acquired or trained sufficient extra labour.

As regards our own new works, I am happy to report that our architect, Mr. E. R. Barrow, F.R.I.B.A., reports that they are progressing quite satisfactorily, the builders being the well-known contractors, Messrs. Walter Lawrence & Son, Ltd. There is, of course, unfortunately a shortage of

bricklayers, but I understand that those who are there are working quite satisfactorily, though the shortage of labour will necessarily delay the completion of the works to a period later than that which was anticipated when the contract was signed.

We are adopting a form of furnace which was decided upon after inspection of several different works in England and Scotland, which, by the courtesy of my brother manufacturers, I was allowed to visit in company with our chemist and technical expert, Mr. J. H. Gardiner, to whose cordial co-operation and technical ability the company are very greatly indebted already, notwithstanding the meagre facilities at his disposal. He is assisting in planning the new works and has suggested many devices with a view to saving labour and improving the processes of manufacture, and I have every confidence that the results will be apparent before we have been in our new works very long.

Hyposol, Limited.

Mr. Stevens mentioned just now the acquisition of the business of Hyposol, Limited. During the war it was in their works that all the mine horn tubes which were made out of our glass were finished and filled ready to be inserted in the horns of the mines, and not one single complaint was ever received from the Admiralty as to the efficiency of either of our glass or of Hyposol's workmanship. By the acquisition of the Hyposol business, we shall be in a strong position as regards lamp-blown glassware, especially in cases where it is essential to employ tube of the highest quality and of the special properties of some of the glasses which we are now manufacturing. Many of the Hyposol staff are highly trained, and the output of the works during the war was generally recognised as being second to none. By the production of tube in large and increasing quantities in our own works we shall be able to supply the Hyposol works with all their needs, and I have no doubt that the acquisition of the business will prove to be highly remunerative.

Window Department.

The enquiries and orders being received in the Window Department are even greater than had been expected. The termination of the war has brought us an almost overwhelming amount of orders and enquiries for memorials to those who gave their lives for the Empire. We have already completed a large number, but enquiries are still being received. In this department clients are able and willing to wait for the execution of their orders, and we are, therefore, not obliged to refuse orders, as we are on the manufacturing side of the business, on the grounds that we cannot carry them out. We are faced with one difficulty in connexion with this Department, and that is to provide the necessary accommodation for the artists and artisans employed in it, after we leave Whitefriars. It is hoped to secure premises in London, where all the processes can be seen under one roof, as it is not considered desirable that clients should be compelled to go to Wealdstone to discuss designs for stained-glass windows and mosaics or to view the carrying out of work upon which they had decided at a studio in London. I hope from what I have said you will have gathered that I am very optimistic with regard to the present outlook for the company, and when once we have firmly established ourselves in our

new works I see practically no end to the possibilities, provided that the ever-increasing demands on the part of labour for higher wages, which must necessarily be reflected in higher prices, do not lessen the demand for our goods on the part of the purchasing public.

Before I sit down I should like to take this opportunity of expressing my obligation to the members of the staff of the old firm who are carrying on with us under the new company, and very particularly to Mr. Orme, our secretary, who came new to the business when it was taken over from the old firm. He has brought to bear upon our affairs a ripe experience gained in a life-long training in company business, and it is a real pleasure to me to have him associated with me in the daily carrying on of the affairs of the company."

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

June 24, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE following papers were read:—

"On some Rostro-carinate Flint Implements and Allied Forms." By Sir RAY LANKESTER, K.C.B., F.R.S.

A series of rostro-carinate flint implements are described and figured in this paper from various localities, including one from the lower Palæolithic gravel of the valley of the Oise (France). It is shown that the form exhibited by the "Norwich test specimen," with ventral plane, dorsal plane or platform, anterior rostrum, with dorsal carina or keel, is modified in some of the specimens here figured by the "flaking away" of the ventral plane and by the hook-like curvature of the rostrum. A large sub-crag example is described, in which only one of the characteristic features of the type, namely, the great ventral plane, is retained—the implement serving as a very efficient "jack-plane." The evidence of the manufacture of these implements by a series of humanly directed blows is indicated by the illustrative drawings.

"A Re-examination of the Light Scattered by Gases in respect of Polarisation. I.—Experiments on the Common Gases." By Lord RAYLEIGH, F.R.S.

Re-determinations are given of the relative intensity of the two polarisations in the light scattered at right angles by pure gases. The paper is chiefly concerned with developing accurate experimental methods. The values obtained are as follows:—

Gas. Intensity of weak component polarisation
(Strong component = 100.)

H ₂	4.51
N ₂	4.74
Air	5.68
O ₂	10.1
CO ₂	12.4
N ₂ O	16.1

"Influence of Temperature on the Rigidity of Metals." By A. MALLOCK, F.R.S.

The experiments here described were carried out at the Davy-Faraday Laboratory, as a con-

tinuation of a somewhat similar set on the temperature variations of Young's Modulus (*see Proc. R.S., A*, vol. 95).

The method adopted in the present series depended on the determination of the periods of a torsion balance whose restitutive couple was given by the rigidity of a specimen of the metal tested at various temperatures.

The coefficients of temperature-variation found for rigidity agreed with those for Young's Modulus in so far that in both cases the variation diminished as the melting-point of the metal increased.

The chief value, however, of the present experiments was in showing that the natural plasticity or internal friction of metals (which leads to what has sometimes been called hysteresis) was even more affected by temperature than were the coefficients of elasticity, and that the value of "rigidity" obtained from the observed periods was very appreciably affected by the variation of plasticity. For this reason the numerical results are not given in the paper, but the method of experiment is described, and the nature of the errors introduced by the change of plasticity is stated.

A further series of experiments is in preparation, in which the plasticity will be recorded as well as the other elements in the problem.

In the structural use of metals, the variation of plasticity, *i.e.*, the limits of elastic rigidity, will probably be found more important than the change of the actual rigidity.

"A Study of Catalytic Actions at Solid Surfaces. V.—The Rate of Change Conditioned by a Nickel Catalyst and its Bearing on the Law of Mass Action." By E. F. ARMSTRONG, F.R.S., and T. P. HILDITCH, D.Sc.

The hydrogenation of selected simple organic compounds containing one ethylenic linkage has been studied with reference to the indications of a linear relation between the amount of hydrogenation and time which were observed in the case of mixtures of unsaturated glycerides (Part I of this series).

It is now found that this relation, in the case of methyl and ethyl cinnamates, safrol or anethol (when hydrogenated in the liquid state in presence of nickel at 140° or 180° C.), takes a linear form for at least 60 per cent and in most cases of 80 to 90 per cent of the whole action.

The interpretation of the mechanism of the action which the authors deduced from the work on unsaturated glycerides thus receives experimental confirmation.

Further experiments illustrate the manner in which the linear graphs for absorption of hydrogen/time may be transformed into curves, generally of a logarithmic type, by the influence of external conditions.

The analogies between these variants of the normal hydrogenation action and similar influences in enzymic hydrolysis is discussed.

The general results of the investigations dealt with in this series of papers are discussed from a theoretical standpoint, with particular reference to the modern development of de la Rive and Marcet's "intermediate compound theory of catalysis, to the different points of view of catalysis taken at present by physicists and by chemists, and to the work of Lord Rayleigh, W. B. Hardy,

and Langmuir on the chemical nature of "adsorption," the latter effect involving the concentration of a single layer of molecules at a surface.

"Tidal Friction in Shallow Seas." By H. JEFFREYS, D.Sc.

In a recent paper G. I. Taylor has shown that the friction of the tidal currents in the Irish Sea over the bottom causes enough dissipation of energy to account for about 1/50 of the known empirical secular acceleration of the moon. This suggests that other and larger shallow areas within strong tidal currents will contribute a still greater amount to the dissipation of energy, and in the present paper the chief shallow seas of the earth are treated separately. The greatest dissipation is found to take place in the Bering Sea, the Yellow Sea, and the Strait of Malacca. Altogether enough is found to account for about 80 per cent of the secular acceleration, leaving a balance to be explained by currents in fjords and along the open coast.

"Arc Spectra in Vacuo and Spark Spectra in Helium of Various Elements." By Prof. J. C. MCLENNAN, F.R.S., J. F. T. YOUNG, M.A., and H. J. C. IRETON, M.A.

(i) The vacuum arc spectra of antimony, bismuth, calcium, magnesium, silver, and copper, and the spark spectra in helium of antimony, bismuth, aluminium, cadmium, lead, magnesium, thallium, and tin have been investigated in the region below $\lambda = 1850 \text{ \AA.U.}$

(ii) The measurements of the arc spectra of antimony, bismuth, calcium, and selenium, and the spark spectra of antimony and lead appear to be the first recorded for these elements in this region.

(iii) The work with the vacuum grating spectrograph has resulted in the extension of the vacuum arc spectrum of copper to about $\lambda = 1216 \text{ \AA.U.}$

"Spark Spectra of Various Elements in Helium in the Extreme Ultra-Violet." By Prof. J. C. MCLENNAN, F.R.S., and A. C. LEWIS, M.A.

In this investigation the spark spectra in helium of the elements: silicon, tellurium, molybdenum, and zirconium, have been determined for the spectral region between $\lambda = 1900 \text{ \AA.U.}$ and $\lambda = 1600 \text{ \AA.U.}$

"Low Voltage Ionisation Phenomena in Mercury Vapour." By K. H. KINGDON.

(i) By the use of a magnetic field, experimental proof has been given that when mercury vapour atoms are bombarded with electrons possessing volt-velocities greater than 4.9, the atoms may be ionised by these collisions.

(ii) An attempt has been made to explain the experimental results of Davis and Goucher on the basis of the results obtained.

(iii) Arguments are presented for showing that the production of ions in mercury vapour at this voltage is not so definitely at variance with the Bohr theory as might be at first thought.

(iv) The experiments go to show that the low-voltage ionisation is not due to ionisation by successive impacts, but that perhaps in order for a 4.9 volt collision to produce ionisation, the velocity of the impinging electron must bear some definite orientation with regard to the orbit of the electron which is to be ejected from the atom.

"Electrification of an Insulated Lens and Allied Problems treated by the Stream Function." By Sir GEORGE GREENHILL, F.R.S.

"Simultaneous Values of Magnetic Declination at Different British Stations." By C. CHREE, F.R.S.

A comparison is made of corresponding diurnal variations of magnetic declination at Eskdalemuir and Kew Observatories.

Mean monthly, daily, and hourly values of declination at Eskdalemuir, Stonyhurst, Falmouth, and Kew are compared. The results are also given of the measurements of a large number of irregular declination changes at the several stations.

It is found that the differences between different stations increase with the amount of magnetic disturbance, and that if accurate information is desired as to magnetic declination anywhere in the field, observations taken on disturbed days should not be relied on. It is thus important that observatory records should be consulted before the results of field observations are accepted.

A number of results are obtained as to the relative amplitudes of irregular declination changes at the several observatories.

"Symmetrisable Functions and their Expansion in Terms of Biorthogonal Functions." By J. MERCER, M.A., D.Sc.

"Reduction of Error by Linear Compounding." By W. F. SHEPPARD.

The paper deals with the general problem of improving an observed quantity, which contains an unknown error, by adding to it a linear compound (linear function) of other observed quantities, called auxiliaries, the coefficients in the added portion being chosen so as to make the mean square of error of the whole a minimum. This is a generalisation of the special problem of finding the improved value when the auxiliaries are the differences, of sufficiently high order, of a set of quantities.

The treatment of the problem is simplified by brief statement of general theorems, and by a theory of conjugate sets of quantities. The fundamental theorem for reduction of error, from which others are easily derived, is that the mean product of errors of the improved value and each auxiliary is 0. If u_0, u_1, u_2, \dots is a set of quantities containing errors, the conjugate set consists of quantities y_0, y_1, y_2, \dots equal in number to the u 's and connected with them by linear relations and such that the mean product of errors of u_r and y_s is 1 if $r=s$, and 0 if r and s are different. If the successive differences of the u 's (commencing with a u) are regarded as a set, the conjugate set consists of sums, of successive orders, of the y 's. The improved value of any linear compound of members of a set, using those after the first k as auxiliaries, is a linear compound of the first k of the conjugate set.

The object is to arrive at formulæ suitable for numerical calculation.

"Plane Stress and Plane Strain in Bipolar Coordinates." By G. B. JEFFERY.

The solution is given for a flat elastic plate, bounded by two circles, when under stresses applied over its boundaries. Curvilinear coordinates are employed for which the coordinate

curves form a double set of orthogonal coaxial circles. Important particular cases are: (1) a circular plate with an eccentric circular hole; (2) a semi-infinite plate bounded by a straight edge with a circular hole; (3) an infinite plate containing two circular holes.

The differential equation of the stress function is solved for these coordinates, and the stress function is obtained for given arbitrary stresses applied over the boundaries, and expressions are deduced for the stresses, and displacements produced at any point of the plate.

In illustration of the general method, the following problems have been specially considered: (1) a pipe with eccentric bore under given internal and external fluid pressures; (2) a plate with an unstressed straight edge and a circular hole under a uniform normal pressure; (3) a plate with a straight edge under a tension parallel to that edge, with an unstressed circular hole. The first two problems are solved in finite terms and the third in series, from which numerical tables are computed.

"The Tidal Motion in the Irish Sea, its Currents and its Energy." By R. O. STREET.

Certain general relations are obtained from the Laplacian dynamical theory connecting the form of the tidal wave and the magnitude of the surface current on a sea of limited extent rotating with the earth. In continuation of a former paper, these are applied to the recorded data for the Irish Sea, and the agreement is found to be fairly satisfactory. A second approximation to the hydrodynamical problem for a rotating tidal basin is then effected, and by means of the relations thus obtained, the mean rates of transfer of water and of energy across certain vertical sections placed transverse to the direction of the flood stream in the Irish Sea are computed from the existing hydrographical data. The results show that there is a residual flow of water northwards through this region of such magnitude that the Irish Sea would empty itself through the North Channel about three times a year, while the tidal flow of energy from all causes which takes place into this area is at the mean rate of about 6×10^{11} ergs per second. The result of this estimate of flow of energy into the area is in general agreement with an independent one made recently by Mr. G. I. Taylor, *Phil. Trans.*, A, 1919, ccxx., pp. 1-33. If we could assume that this energy is all dissipated, the result would be about 250 times the viscous dissipation calculated directly by the writer in a previous paper (*Roy. Soc. Proc.*, A, 1917, xciii., pp. 348-359), on the assumption of smooth laminar tidal motion throughout the region.

"The Catalytic Activity of Copper." By W. G. PALMER.

Simple apparatus is described for the measurements by chronograph records of the reaction velocities at different temperatures of a typical catalytic action—that of the dehydrogenation of alcohol by copper. Details are given of the methods used in preparing a reproducible contact material. After oxidation and reduction a second time, the copper showed an activity of unchanged value.

It is shown that copper prepared electrolytically is quite inactive as a catalyst, in spite of great variation in the conditions of its deposition.

Copper reduced from its oxide was active at temperatures above 200°C ., but this activity depended on the temperature at which the metal was reduced from its oxide.

Two curves have been constructed, showing the relation between temperature and catalytic reaction velocity for: (a) copper formed by reduction at the lowest possible temperature; (b) copper formed by reduction at 205°C .

The curve (a) shows a sharp change of direction at about 260°C ., but the curve (b) is nearly a straight line, there being only a slight convexity towards the velocity axis. The form of these curves and the mechanism of the reaction are tentatively discussed and suggestions made for a continuation of the work.

"The Origin of the 'Cyanogen' Bands." By S. BARRATT.

(i) Observations have been made of the spectra of the flames of a number of gases containing carbon, hydrogen, nitrogen, and oxygen.

(ii) The cyanogen bands are strongly developed in the coal-gas-nitrous oxide flame.

(iii) Evidence has been obtained that they are entirely absent from the hydrogen-nitrous oxide flame, if all traces of carbon are excluded, and it appears to follow that the presence of carbon is essential to their production.

(iv) The appearance of the cyanogen bands is, under appropriate conditions, a more delicate test for carbon than that of any of the other bands associated with that element. On the other hand, this spectrum is not necessarily developed when both carbon and nitrogen are present.

(v) The conclusion of Grotian and Runge that the cyanogen spectrum is to be attributed to nitrogen is shown to rest on assumptions which are not confirmed in the present investigation.

(vi) The cyanogen spectrum provides a very delicate test for the presence of compounds of nitrogen when admitted in the form of a gas to hydro-carbon flames burning in air, since elementary nitrogen does not appear, under ordinary circumstances, to be effective in producing the cyanogen bands in such flames.

(vii) The intensity of the cyanogen bands when carbon compounds are admitted to the hydrogen-nitrous oxide flame bears no simple relation to the amount of carbon thus added.

"Effects of Electron Collisions with Atmospheric Neon." By F. HERTON, Sc.D., and ANN C. DAVIES.

The critical velocities for electrons in neon were investigated by methods similar to those employed with helium and argon. It was found that neon differed from these gases in showing more than one critical velocity, both for radiation and for ionisation, these critical velocities being detected under conditions such as to preclude the possibility of any of them being due to the displacement or removal of a second electron from the atom. The critical values observed were:—

A minimum radiation velocity of 11.8 volts.

A minimum ionisation velocity of 16.7 volts.

A second radiation velocity of 17.8 volts.

A second ionisation velocity of 20.0 volts.

A third ionisation velocity of 22.8 volts.

In obtaining these values special experiments were made to determine the correction to be added to the potential differences accelerating the elec-

tron stream, so as to give the velocity of the electrons actually producing the effect observed at a critical point.

The experiments led to the conclusion that the radiation velocity of 11.8 volts is associated with the ionisation velocity 16.7 volts, and that the radiation velocity 17.8 volts is associated with the ionisation velocity 22.8 volts. These four critical velocities would be accounted for by the presence of two different kinds of atoms in the gas, either two different elements or two isotopes with different arrangements of the electrons surrounding the nucleus. The additional ionisation at 20.0 volts, which was not so strongly marked as the other effects, may perhaps be associated with a radiation velocity almost identical with one of those mentioned, or it may be due to a secondary effect arising from atoms having a radiation velocity of 20.0 volts. This latter possibility is discussed in the paper.

"Occurrence of Diatoms on the Skin of Whales." By A. G. BENNETT. With an Appendix by E. W. Nelson, M.A.

Mr. Bennett states that the skin of certain fin whales and blue whales captured in Sub-Antarctic waters is discoloured by a superficial film of a buff colour, resembling in tint the coloured bands often observed on floating ice. Whales thus affected are nearly always fat. Microscopic examination showed that this film consists of immense numbers of diatoms.

The fat individuals are probably those which have spent some time in the far south, where the supply of whale food is very abundant during the summer. There is reason to believe that the thin individuals are recent arrivals from warmer water. The skin of these thin specimens appears to be free from any noticeable film of diatoms; their light parts are thus white, instead of having the yellow tinge which has given rise to the name "Sulphur-bottom," applied by the whalers to whales in which the light parts are yellowish.

The cutaneous film of Antarctic Sulphur-bottoms may be composed of the same diatoms as those which form the coloured bands on ice. If it can be proved that the outer surface of whales may become colonised by diatoms occurring in the waters frequented by them, the extended investigation of their skin may throw important light on their migrations by the study of the geographical distribution of the species of these microscopic organisms found on them. The demonstration of the nature of the deposit is further of interest in showing that whales differently coloured do not necessarily belong to distinct species. This may have a definite bearing on the question of the identity or otherwise of the species found in different localities.

Mr. Nelson's detailed examination of the specimens collected completely confirms Mr. Bennett's original observation as to the nature of the film. With the exception of one sample (which may possibly have been contaminated by diatoms from another source) all the films represented consist of diatoms of a single species, belonging to the genus *Cocconeis*, the members of which are usually found attached to submerged objects. The *Cocconeis* in question is described as a new species, and it thus gives no information with regard to the locality in which the diatom-infection originated.

"An Extension of the Balmer Series of Hydrogen and Spectroscopic Phenomena of very Long Vacuum Tubes." By R. W. WOOD, For. Mem. R.S.

"Moving Striations in Neon and Helium." By F. W. ASTON, M.A., D.Sc., and T. KIKUCHI.

When an induction coil spark is passed through a spectrum tube containing neon, and the discharge observed with a rotating mirror, it is seen to consist of bright striations moving from the anode towards the cathode. When first observed the velocity was found to be roughly that of sound in the gas.

Further investigations now show that this is only a limiting case of a very complex phenomenon. The velocity is found to decrease with increase of pressure, and also to depend on the bore of the tube. The effect of change of temperature has been investigated, and curves are given showing that at constant volume the effect is much greater than the expansion coefficient. At constant pressure the temperature effect only comes in at high temperatures when it is probably due to impurities liberated from the tube.

Helium is found to give much the same sort of results as neon. Experiments with mercury vapour and other gases are also described. No satisfactory theoretical conclusions have yet been arrived at and further experiments are in progress.

NOTICES OF BOOKS.

Techno-Chemical Receipt Book. Compiled and Edited by WM. T. BRANNT and WM. H. WAHL, Ph.D. Pp. xxxiii+516. London: Hodder & Stoughton, Warwick Square, E.C.4. 1920. Price 15s. net.

THE editor's aim in bringing this book before the public is to give an accurate and compendious collection of approved receipts and processes of practical application in the industries, and for general purposes. They have purposely excluded all theoretical reasoning and historical detail from the book, thus making it essentially a receipt book.

The book has been arranged alphabetically, but a copious table of contents as well as a good index are included so as to render the reference to any subject or special receipt prompt and easy.

Previous editions have been thoroughly revised, and this receipt book has been brought quite up-to-date.

Bygone Beliefs. By H. STANLEY REDGROVE, B.Sc., F.C.S. Pp. xvi+205. London: Wm. Rider & Son, Ltd., 8, Paternoster Row, E.C.4. 1920. Price 10s. 6d. net.

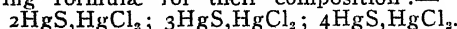
THOSE interested in the early days of Alchemy should read Mr. Redgrove's book on "Bygone Beliefs". He takes the reader back to the mediæval times, and gives him representations of the superstitions and thoughts that were characteristic of the age.

The book is divided into twelve chapters each dealing with a belief or superstition of olden times, the explanations of which are helped by the interspersed of many illustrations.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires de l'Académie des Sciences. Vol. clxx., No. 25.

PRECIPITATION OF MERCURIC SALTS BY HYDROGEN SULPHIDE.—MM. Pierre Jolibois and Pierre Bouvier.—When a solution of a mercuric salt is acted upon by sulphuretted hydrogen, a gradation in the colour of the precipitate can be noticed. These precipitates pass through a series of colourations from white to black. Polek and Gorki (*Ber.*, 1888, xxi, 2412), have given the following formulæ for their composition:—



The authors have studied the composition of these coloured precipitates by using a solution of mercuric chloride of varying known strength precipitated by a 1/20th normal solution of sulphuretted hydrogen. The precipitate thus obtained was filtered off, dried, and the content of sulphur obtained by first oxidation with aqua regia and then precipitation as barium sulphate. The following table gives the result of their investigations:—

Strength of H ₂ S solu.	Strength of HgCl ₂ solu.	Colour of precipitate	Content of sulphur.	Theory.
Normal.	Normal.		Per cent	Per cent
1/20	1/40	black	13.8	
1/20	1/20	black	13.9	HgS
				=13.8
1/20	1/16	black	13.5	
1/20	1/13.2	dark brown	12.7	2HgS, HgCl ₂
				=8.7
1/20	1/11.5	reddish brown	10.1	
1/20	1/10	yellow	9.2	
1/20	1/9	white	8.9	
1/20	1/8	white	8.6	

This table shows that the composition of the precipitate remains constant while there is an excess of sulphuretted hydrogen or an excess of mercuric chloride, corresponding in the first case to the formula HgS, and in the second to 2HgS, HgCl₂. As to the intermediate precipitates, their composition varies proportionally with the content of mercuric chloride between the neighbouring limits.

NOTES.

THE Secretary of the Department of Scientific and Industrial Research begs to announce that the Research Association for the Silk Industry has been approved by the Department as complying with the conditions laid down in the Government scheme for the encouragement of industrial research. As the Association is to be registered as a non-profit sharing company, the promoters have applied to the Board of Trade for the issue of a license under Section 20 of the Companies (Consolidation) Act of 1908. The Secretary of the Committee engaged in the establishment of this Association is Mr. A. B. Ball, The Silk Association of Great Britain and Ireland, Kingsway House, Kingsway, W.C.

ACETALDEHYDE.—The employment of this very useful material is likely to be extended in the near future to a considerable extent. The drawback up to the present has been the difficulty of transport. The polymerised material paraldehyde, however, does not suffer from the same drawbacks and can be conveyed without risk. Acetaldehyde is partially polymerised into this product and it can be regenerated very simply. The commercial paraldehyde made in Canada is approximately a mixture of 90 per cent paraldehyde and 10 per cent unpolymerised acetaldehyde. It is made synthetically from acetylene and is, therefore, of a very high degree of purity. Messrs. A. Boake, Roberts & Co., Ltd., of Stratford, E.15, are the selling agents for both commercial grade and the B.P. The commercial variety comes over from Canada packed in drums holding about 900lbs. of the liquid. The B.P. material is packed in Winchestersters.

THE CHEMICAL SOCIETY.—The lecture room at Burlington House, W., having proved to be entirely inadequate to accommodate the large audiences which attend the lectures, that on "Helium", by Professor J. R. McLellan, on June 17, was held in the lecture theatre of the Institution of Mechanical Engineers, by the courtesy of its Council. Sir J. J. Dobbie presided over an audience of nearly 250 and announced that the Emil Fischer Memorial Lecture would be given by Dr. M. O. Forster on October 21 next. He also made an appeal to British chemists to send donations (by July 31 at latest) in support of the memorial being raised by their French colleague to the memory of C. F. Gerhardt (1816—1856), the well-known French chemist. The subject matter of the lecture included data concerning the occurrence and content of helium in natural gas within the Empire, more particularly in Canada; the designs of the modifications of the Claude plant and process utilised, together with yields and possible applications. Prof. McLellan's latest experiments show that it is practicable to isolate on a commercial scale helium of 97 per cent purity from the natural gas at Hamilton, Ontario, at a cost of less than 2½d. per cubic foot at Hamilton. A fuller account of the lecture will be given in these columns in due course. Sir Richard Threlfall, who spoke on the vote of thanks to the lecturer, stated that his suggestion to use helium in airships was communicated to the Admiralty as early as October, 1914, and that he was led thereto by press notices to the effect that the Germans were contemplating the use of an unflammable gas. A search into the literature, especially into the investigations of Prof. C. Moureu on the dissolved gases in the springs of France, enabled him to show that the use of helium by the Germans was improbable, and then to present in outline a definite scheme of large-scale production from natural gas at Fredonia, Kansas, U.S.A., where the gas was known to be comparatively rich in helium. After a very full investigation, the Admiralty decided, in August, 1915, not to proceed with the scheme, but when America came in, all the information which had accumulated was passed on to that country.

THE BOHEMIAN GLASS INDUSTRY.—The glass factories are now overwhelmed with orders, partly

on account of the conditions of exchange and partly owing to the large business which resulted from the fairs of Leipzig and Lyons. In trade circles, however, the opinion is held that after two years of such activity over-production is bound to follow. Japan is to be regarded as a dangerous competitor; in 1914 that country had 463 glass factories and about 9000 workers, in 1917 there were 832 factories and 17,000 workers. In consequence of this competition, the Indian and most of the markets in the Near East are probably lost for good. New works have been erected in Belgium, the Ukraine, Rumania and Poland, and in north-west Bohemia alone 19 large new companies have recently been founded. All these facts point to a quick reaction for the local glass industry.—(*Z. angew. Chem.*, April 20, 1920.).

ANNOUNCEMENT.—The Lord President, as President of the Council for Scientific and Industrial Research, has appointed Dr. J. S. Flett, F.R.S., at present Assistant to the Director in Scotland, to be Director of the Geological Survey and Museum. Dr. Flett succeeds Sir Aubrey Strahan, K.B.E., F.R.S., who retires this month, when Mr. G. W. Lamplugh, F.R.S., Assistant to the Director in England, also retires.

MILK PRODUCTS IN AMERICA AND EUROPE.—A recent investigation of this field is given in a report by W. Dempster, published in the *New Zealand Journal of Agriculture*, 1920, xx., 97-109. Milk powder is manufactured by the use of heated rolls, or by spraying the previously concentrated milk into a hot chamber. In addition to its other uses in the food industries, skim milk powder or dried skim milk is used with butter in reconstituting milk and cream during seasons of scarcity of fresh milk. In the manufacture of reconstituted cream, the proper amounts of skim milk powder and water are placed in a jacketed vat and are intimately mixed by a propeller which revolves at a high speed. The speed is reduced, the proper amount of butter added, and the temperature of the mixture gradually raised to 145° F., kept constant for twenty to thirty minutes, then lowered to 135° F. The mixture is next put through a homogeniser, and immediately cooled to 45° F. In reconstituting milk, the skim milk powder and water are mixed as just described; the butter, which has been heated to a temperature of 120° F., is now forced through a spray nozzle which lies beneath the surface of the liquid; the finely divided butter fat is uniformly distributed throughout the reconstituted milk. Whole milk powder apparently does not keep well; it seems to require cold storage, e.g., 0 to -8° F., for its preservation. During the war, the production of lactose or sugar of milk increased enormously, since large amounts of that compound were used in the manufacture of smoke-shells. The casein industry of America centres in Philadelphia; this milk protein may be used as the basis of paints, which may be produced in any desired colour, withstand water, and retain their colour. The shortage of butter in England increased the demand for sweetened condensed milk, which was eaten spread on bread.—*Journal of the Franklin Institute*, June, 1920.

POTASH DEPOSITS IN SPAIN.—(*U.S. Geological Survey Press Bulletin*, No. 443, April, 1920).—Potash deposits were discovered in the Province of Barcelona, Spain, near the villages of Suria and Cardona. They consist of irregular beds of carnallite and sylvinite interbedded with rock salt. Explorations to a depth of several hundred feet show that in the Suria district potash beds occupy an area of not less than 75 acres and occur at depths from 125 to 200 feet. The average combined thickness of the carnallite beds is estimated to be about 56 feet, and of the sylvinite about 13 feet. The Cardona upper beds are interbedded with gypsum and clay, but the lower beds contain nearly pure white salt, which is that principally mined. After the discovery of potash at Suria, these Cardona beds were searched for potash, and nearly pure sylvite was found. Estimates for the area prospected place the quantity of carnallite at 2,550,000 tons and of sylvinite at 1,150,000 tons.

APPOINTMENT.—The Council of the University of Swansea have appointed Mr J. E. Coates, D.Sc. (B'ham), and M.Sc. (Wales) for the past ten years an Assistant Lecturer on Chemistry at the University of Birmingham, Professor of Chemistry at a salary of £800 per annum. He was a student at the University of Wales, and also studied in Germany and London.

Mr. G. B. BROOK, Lecturer in Nonferrous Metallurgy to the University of Sheffield, has accepted the responsible position of chief chemist to the British Aluminium Company. Mr. Brook's connection with the light industries of Sheffield extends over thirty years. He was trained under Mr. A. H. Allen, Public Analyst for Sheffield and the West Riding, and was the first lecturer in non-ferrous metallurgy at the Sheffield University. During the War he was closely identified with the work of the Sheffield Munitions Committee and subsequently in the establishment of the Wounded Officers' Training Department in nonferrous metallurgy. His departure will be a distinct loss to the city of Sheffield.

NOTICE.

OWING to the greatly increased cost of printing and paper, and the advance in the postal rates, we have been compelled to raise the price of the **CHEMICAL NEWS** from 4d. to 6d. (by post 7d.). The new subscription rates are as follows:—

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3146.

EDITORIAL.

THE following papers have been received for publication, and will be inserted as space permits:—

"The Constitution and Structure of the Chemical Elements." "The Number 23." A mathematical proof is given that a mass of 23 (from which emanates one valence) takes a prominent part in the formation of all elements of greater mass than itself.

"The Five Main Principles in the Constitution and Structure of the Chemical Elements." This paper is chiefly concerned with the fifth principle, viz.:—Each of the heavier elements is formed by the union of simpler elements (which are indicated in each case by mineralogical and chemical facts combined.) A proof is given that the observation of this principle is not due to a series of accidents.

"The Constitution and Structure of the Radio-Active Elements." It is shown that there is a great probability that hexadic titanium is the main constituent of radio-elements. There is no claim that this particular deduction is proved to be true, because there are not sufficient facts available to make possible the application of the theory of mathematical probability.

(By Hawksworth Collins, Stubbington House School, Fareham, Hants.).

DISTRIBUTION OF ACETIC ACID BETWEEN WATER AND CHARCOAL.

By ALWYN PICKLES.

ACETIC acid solutions of different normality were used, 100 cc. at a time. Charcoal was added, 5 grms., and equilibrium between the two phases obtained. Complete equilibrium took several hours, but most of the sorbtion took place very rapidly.

The concentration of the aqueous phase was obtained by filtering off charcoal and titrating known volumes of the filtrate, with N/10 caustic soda. Knowing the real density of the charcoal used and original normality of acid, the concentration per cc. of charcoal readily followed.

Experiments were done with several kinds of charcoal in varying states of division. The effect of temperature was also studied.

Concentrations are given in mols. per cc.

I. *Fruit Stone Dust.* Density 1.70.

Acid Normality.	C (Water) 10 ⁻⁵			C (Charcoal) 10 ⁻⁴		
	12°	30°	50°	12°	30°	50°
3	238	251	262	214	167	129
2	155	160	166	154	136	115
1	68	77	80	110	78.2	68
0.5	29	—	—	70	—	—

II. *Animal Charcoal.* Density 2.80. Per cent C=21.

Acid Normality.	C (Water) 10 ⁻⁴			C (Charcoal) 10 ⁻⁴		
	12°	30°	50°	12°	30°	50°
3	23	26.4	26.4	392	202	202
2	15	16.8	17	280	179	168
1	6	7.8	8	224	123	112
0.5	2	—	—	167	—	—

III. *Birch Dust.* Density 1.46.

Acid Normality	C (Water) 10 ⁻⁵			C (Charcoal) 10 ⁻⁴		
	12°	30°	50°	12°	30°	50°
3	260	254	...	115	134	...
2	166	160	...	99	117	...
1	74	64	...	76	105	...

IV. *Birch Coarse.* Density 1.47.

Acid Normality.	C (Water) 10 ⁻⁴			C (Charcoal) 10 ⁻⁴		
	12°	30°	50°	12°	30°	50°
3	25	25	...	147	147	...
2	16	17	...	118	88	...
1	7.3	7.2	...	79	80	...

It is seen from the above that:—

- (1) More acid is removed relatively from dilute solutions.
- (2) Concentration per cc. of charcoal depends on the kind of charcoal and on its state of division.

In the preceding cases, the acid and charcoal had been in contact at least 24 hours at 10°-12° C. Hence, surface and interior effects may be assumed as complete and that equilibrium existed between polymerised and simple molecules. Increase of temperature disturbs this equilibrium, the tendency being for polymerised molecules to break down into simpler ones. The acid concentration of charcoal therefore diminishes.

If, however, acid and charcoal are only together for a short period, increase of temperature increases the acid concentration in charcoal to a slight extent. This is due to the hastening of the interior effect otherwise not complete. Animal charcoal is an exception. It removes the acid almost entirely by adsorption. Though such charcoal is porous in the mass through presence of such things as calcium phosphate, the actual carbon particles have not that complex structure which characterises wood charcoal.

Since the charcoal and aqueous phases are immiscible it is instructive to apply the distribution equation.

$$\frac{C^{\text{Charcoal}}}{C^{\text{Water}}} = K$$

The values of 'n' giving the most consistent values for K vary with the charcoal used and also its state. Thus:—

I. *Fruit Stone.* n=1.97.

12°	K=0.202	K=0.205	0.206	0.208
30°	n=1.8	K=0.144	0.145	0.142
50°	n=1.76	K=0.135	0.139	0.136

II. *Animal Charcoal.*

12°	n=2.4	K=0.308	0.360	0.307	0.316
30°	n=2.1	K=0.220	0.225	0.219	—
50°	n=2.0	K=0.209	0.210	0.209	—

III. *Birch Dust.*

12°	n=2.6	K=0.197	0.199	0.201
50°	n=2.3	K=0.281	0.281	0.245

IV. *Birch Coarse.*

12°	n=2.1	K=0.207	0.206	0.205
50°	n=2.0	K=0.196	0.184	0.197

The value for n given in Thorpe's "Dictionary of Applied Chemistry," vol. ii., Colloids, is 2.35. This is evidently an average value.

The above work has been repeated by a class of chemistry students and the above results confirmed within a very small margin.

A STUDY OF DOLOMITES.

By C. L. HARDING, J. B. SHUMAKER, and A. W. ROTHROCK.

DEODAT DOLOMIEU was born in Dolomieu, France, June 23, 1750, and died November 16, 1801. In infancy he was created a Knight of Malta. He seemed precocious in many directions. When nineteen years of age he quarrelled with a companion and killed him. He was condemned to death for the crime, but after nine months' imprisonment, he was pardoned on account of his youth. He early became interested in geology and mineralogy, and wrote some important treatises on his favourite subjects, especially while residing in Metz, the interesting old capital of Lorraine.

He discovered dolomite while making an extended tour and observations among the Alps in 1789-90. The mineral was first described by him in 1791, and the name was bestowed upon it in honour of the discoverer.

The dolomite mineral and rock are important from both a theoretical and practical standpoint. Much work has been done upon them, and the mineral can be artificially produced by a number of different methods.

Marignac was probably the first to make it artificially. His method was to heat calcium carbonate and a solution of magnesium chloride to 200° under a pressure of fifteen atmospheres. In a closed gun barrel J. Doroche heated porous limestone and dry magnesium chloride to about 1200°. The vapour of the chloride permeated the porous limestone, which was partially transformed into dolomite. In a similar way, it has been suggested, the heat in the neighbourhood of volcanoes may produce the mineral and rock.

One of the simplest methods was devised by C. Sainte-Claire Deville. He saturated chalk with a solution of magnesium chloride and heated the mixture upon a sand-bath. More or less of the materials change into dolomite.

By heating powdered calcite with magnesium sulphate to 200° in a closed tube, von Morlot obtained a mixture of dolomite and calcium sulphate. It has been suggested by Haidinger that this reaction accounts for the frequent association of dolomite and gypsum.

T. Sterry Hunt conducted a long series of experiments on the precipitation of calcium and magnesium carbonates, from which he reached the conclusion that dolomite is simply a chemical precipitate. This view has not been generally adopted.

In more recent times, 1909, G. Linck published a report of a new method of making dolomite. He mixed solutions of magnesium chloride, magnesium sulphate, and ammonium sesquicarbonate, and then added a solution of calcium chloride. An amorphous precipitate came down, which on gently heating for some time in a closed tube became crystalline. This had the composition and optical properties of dolomite. Linck believes that his experiment explains the formation of marine dolomite, and that the ammonium salt necessary can easily result from the decomposition of organic substances.

Most of the specimens for this study were received from Ward's Natural Science Establishment, Rochester, New York.

1. *Specimen from New Almadin, California.*—This is a hard, greyish-white variety. It consists of large compact crystals, with one surface coated with a brown deposit. The specific gravity is 2.8.

SiO ₂	0.40	per cent.
Fe ₂ O ₃	8.57	"
Al ₂ O ₃	0.00	"
CaCO ₃	53.58	"
MgCO ₃	37.86	"

100.11 per cent.

2. *Hell Fire Rock, Wahsatch Mountains, Utah.*—The rock is white, crumbly, and fine granular in appearance. The analysis revealed that it is quite a pure sandstone and cannot be classed with the dolomites. The specific gravity is 2.2.

SiO ₂	95.29	per cent.
Fe ₂ O ₃	2.88	"
Al ₂ O ₃	1.68	"
CaCO ₃	0.16	"
MgCO ₃	0.00	"

100.01 per cent.

3. *Specimen from Hurley, Wisconsin.*—The sample contained a number of quartz crystals, also iron pyrite and siderite. The exterior contained a number of dolomite of a pinkish hue, and only the dolomite crystals were taken for the analysis. The specimen proved a fairly good dolomite. We did not determine the specific gravity.

SiO ₂	2.56	per cent.
Fe ₂ O ₃	9.27	"
Al ₂ O ₃	0.00	"
CaCO ₃	48.52	"
MgCO ₃	40.02	"

100.37 per cent.

4. *Specimen from Brosso, Piedmont, Italy.*—It had a peculiar appearance and consisted of large olive-green crystalline lumps, resembling clay balls. They are very compact and are held together by ferric oxide. The specific gravity is 2.91. From the analysis the specimen may be classed as a dolomite.

SiO ₂	4.97	per cent.
Fe ₂ O ₃	6.44	"
Al ₂ O ₃	0.00	"
CaCO ₃	50.46	"
MgCO ₃	37.82	"

99.69 per cent.

5. *Specimen from Georgetown, New Mexico.*—Dull white rhombohedral crystals. The analysis shows the mineral is quite a pure calcite rather than a dolomite. The specific gravity is 2.46.

SiO ₂	0.57	per cent.
Fe ₂ O ₃	0.06	"
Al ₂ O ₃	0.55	"
CaCO ₃	98.32	"
MgCO ₃	0.88	"

100.38 per cent.

6. *Specimen from Lancaster County, Pennsylvania.*—The pure white rhombohedral crystals are a fairly typical dolomite. The specific gravity is 2.31.

SiO ₂	0.48	per cent.
Fe ₂ O ₃	1.58	"
Al ₂ O ₃	1.63	"
CaCO ₃	56.60	"
MgCO ₃	40.50	"

100.79 per cent.

7. *Specimen from Diembachkogel, Styria, Austria.*—It was a typical dolomite with large white rhombohedral crystals with a specific gravity of 2.89.

SiO ₂	0.40	per cent.
Fe ₂ O ₃	1.52	"
Al ₂ O ₃	0.00	"
CaCO ₃	54.39	"
MgCO ₃	43.51	"

99.81 per cent.

8. *A dolomitic limestone from Kasota, Minnesota.*—The specimen was massive, grey, soft and porous, with a reddish coloration on the surface. The specific gravity is 2.61.

SiO ₂	9.41	per cent.
Al ₂ O ₃	1.74	"
Fe ₂ O ₃	0.96	"
CaCO ₃	53.67	"
MgCO ₃	34.82	"

100.60 per cent.

9. *Specimen from St. Louis, Missouri.*—The rhombohedral crystals are on the surface of a light grey compact massive rock. It contains a large amount of silica. The specific gravity is 2.52.

SiO ₂	25.70	per cent.
Fe ₂ O ₃	0.00	"
Al ₂ O ₃	24.65	"
CaCO ₃	47.34	"
MgCO ₃	2.98	"

100.67 per cent.

10. *Specimen from Orange County, New York.*—Pink and white rhombohedral crystals with a specific gravity of 2.74.

SiO ₂	2.59	per cent.
Fe ₂ O ₃	0.57	"
Al ₂ O ₃	0.00	"
CaCO ₃	56.80	"
MgCO ₃	39.39	"

99.35 per cent.

11. *Specimen from Fassathal, Tyrol.*—A dark grey central mass covered with a layer of dark rhombohedral crystals. A mixture of both portions was taken for the analysis. The specific gravity is 2.82.

SiO ₂	0.79	per cent.
Fe ₂ O ₃	0.23	"
Al ₂ O ₃	0.71	"
CaCO ₃	60.32	"
MgCO ₃	38.78	"

100.83 per cent.

12. *Specimen from Columbia, Pennsylvania.*—It is a black rock containing rhombohedral and

irregular shaped crystals, soft and with a bright lustre. The analysis shows it to be a limestone rather than a dolomite. The specific gravity is 2.69.

SiO ₂	0.80	per cent.
Fe ₂ O ₃	0.31	"
Al ₂ O ₃	0.20	"
CaCO ₃	95.08	"
MgCO ₃	3.53	"

99.92 per cent.

13. *Specimen from Lockport, New York.*—Pink and white rhombohedral crystals of a pearly lustre, over a dark grey compact interior. The specific gravity is 2.84.

SiO ₂	0.01	per cent.
Fe ₂ O ₃	2.07	"
Al ₂ O ₃	2.39	"
CaCO ₃	55.78	"
MgCO ₃	39.35	"

99.60 per cent.

14. *Specimen from Freiberg, Saxony.*—The interior is finely granular and marble-like. The rhombohedral crystals on the exterior are brownish in colour. The specific gravity is 2.87.

SiO ₂	0.55	per cent.
Fe ₂ O ₃	11.53	"
Al ₂ O ₃	2.55	"
CaCO ₃	54.37	"
MgCO ₃	31.45	"

100.45 per cent.

15. *Specimen from Cumberland, England.*—The crystals are both rhombohedral and irregular in form. There is a variety of colour, including pink, white, black, brown, and slate; also irregular masses of hard, compact, reddish crystals. The analysis was made from a mixture of the entire specimen. The specific gravity is 2.84.

SiO ₂	6.05	per cent.
Fe ₂ O ₃	8.04	"
Al ₂ O ₃	3.40	"
CaCO ₃	59.43	"
MgCO ₃	22.85	"

99.77 per cent.

16. *Specimen from Lee, Massachusetts.*—It is a hard white rock resembling marble, with small shining rhombohedral crystals. The specific gravity is 2.87.

SiO ₂	0.64	per cent.
Fe ₂ O ₃ and Al ₂ O ₃	0.20	"
CaCO ₃	65.50	"
MgCO ₃	33.64	"

99.98 per cent.

17. *Specimen from Eisfeld, Westphalia, Germany.*—It is composed of large white crystals, irregularly set together, and is accompanied by calcite and chalcopryrite. A few of the crystals are slate grey. The specific gravity is 2.80.

SiO ₂	1.51	per cent.
Fe ₂ O ₃	11.49	"
Al ₂ O ₃	2.28	"
CaCO ₃	61.89	"
MgCO ₃	23.24	"

100.41 per cent.

18. *Specimen from Niagara Falls, New York.*—Irregular shaped crystals, pink, yellow, slate, and black, accompanied by calcite and selenite. The specific gravity is 2.8.

SiO ₂	1.01	per cent.
Fe ₂ O ₃	1.26	"
Al ₂ O ₃	5.42	"
CaCO ₃	66.41	"
MgCO ₃	26.33	"

100.43 per cent.

19. *Specimen from Cumberland, England.*—The interior consists of a mass of white crystals and the surface is large, red, and irregular crystals. We mixed together both kinds for the analysis. Specific gravity 2.91.

SiO ₂	0.68	per cent.
Fe ₂ O ₃	11.09	"
Al ₂ O ₃	2.85	"
CaCO ₃	57.36	"
MgCO ₃	28.42	"

100.40 per cent.

20. *A dolomitic limestone from Rochester, New York.*—A slate-coloured rock with brown crystals on the surface. The specific gravity is 2.79. Both portions of the specimen were ground together for the analysis.

SiO ₂	3.05	per cent.
Fe ₂ O ₃ and Al ₂ O ₃	0.31	"
CaCO ₃	43.75	"
MgCO ₃	52.96	"

100.07 per cent.

The magnesium carbonate exceeds the amount of calcium carbonate.

Most of the twenty specimens here described may fairly be classed as dolomites; yet the term is rather a vague and loose one, and the mineral varies in composition in rather wide limits.

Cornell College, Mount Vernon, Iowa,
June 18, 1920.

PRODUCTION OF ATTAR OF ROSES IN BULGARIA.

By GRAHAM H. KEMPER.

DURING the 12 years prior to the first Balkan War, that is, from 1900 to 1912, the manufacture of attar of roses in Bulgaria attained its highest development. During that period a large number of up-to-date factories equipped with modern steam stills were erected. The total area planted to roses increased to more than 20,000 acres. Owing to the three wars in which Bulgaria has taken part since 1912, the industry of rose culture for the production of attar of roses has experienced a decided setback. It is estimated that the present acreage planted to roses is not more than 15,000.

The average annual production of attar of roses during the period from 1900 to 1912 was about 126,800 ounces. The production fell to 85,000 ounces in 1917, 85,000 ounces in 1918, and 52,000 ounces in 1919, and it is predicted that the present year's yield will show a further decrease.

During the war, owing to the fact that Bulgaria was cut off from the principal markets—New York, London, and Paris—the stocks of attar of

roses remaining unsold increased until they reached a total of about 275,000 ounces, about 40 per cent of which is said to have been of inferior quality. About one-third of this total available stock was sent to the United States early in 1919 in part payment for flour imported from the United States; also some 17,000 ounces were shipped to the United States during the last quarter of the year. It is estimated that the present available stock in Bulgaria hardly exceeds 50,000 ounces, worth about \$500,000.

It is stated by one of the best-known producers that under existing conditions the production of attar of roses is not a paying industry. Owing to the high prices for other farm products, at least 5000 acres of rose gardens have been abandoned and the land planted to more remunerative crops, especially tobacco. Centralisation, by the formation of a syndicate for the purpose of eliminating unnecessary expenses, is spoken of as the only course that will save the industry.—*American Journal of Pharmacy*, June, 1920.

DEVELOPMENT OF KAURI GUM INDUSTRY IN NEW ZEALAND.

By ALFRED A. WINSLOW.

SINCE the close of war more attention has been given to the development of the kauri-gum industry in New Zealand than any time during the past five years, with the result that it seems probable that greater quantities of kauri gum and its by-products will be produced than heretofore.

Oil from Kauri Peat Swamps.—There are very extensive kauri peat swamps in New Zealand that have been placed at the disposal of interested parties by the New Zealand Government on a leased basis. The present area for which the Governor General by Order in Council may set apart for the development of this industry is 10,000 acres on a basis of leases for 42 years, with no party to receive a lease exceeding 3000 acres. The lessees have to pay a low rental and also a royalty on kauri oil and other valuable products obtained.

The New Zealand Peat Oils (Ltd.) have taken one grant of 3000 acres, and are now developing it with reasonably good prospects of success, having tested four samples taken from different depths of the swamp which yielded an average of 29 gallons of crude kauri-gum oil to the ton, with a yield of 4300 cubic feet of gas per ton. This company proposes to push the development of this industry during the coming year.

Kauri Gum Extraction and Grading.—A new method of gathering and grading kauri gum has lately been undertaken, whereby kauri peat swamps that are thoroughly pregated with kauri gum in different stages of decomposition can be worked with reasonably good success, according to late reports. It is claimed that if this process succeeds, as indicated at present, there can be more kauri gum secured from the deposits in the North Island than has been secured to date, though of an inferior grade to that which has been gathered.

It is proposed to grade this kauri gum into about three or four grades according to size, which means largely according to the degree of composi-

tion. It is claimed any grade would be sufficient in quality for the manufacture of the lower grades of varnishes and similar products, and would be exceptionally good for the manufacture of linoleums and that line of goods; and it is expected that these qualities of kauri gum can be produced in such quantities as to be sold for a very much more reasonable price in proportion to what kauri gum has been sold for heretofore.

Production of Kauri Gum.—The production of kauri gum during the seven years previous to the beginning of the war averaged not far from 8000 tons per year, while since that time it has scarcely averaged 4000 tons, and during the year ended, March 31, 1919, only amounted to 2338 tons. Of the output of 8473 tons for 1914 the United States took 4531 tons, the United Kingdom 3335 tons, Germany 373 tons, and the remainder was well scattered over 10 other countries; while for the year ended March 31, 1919, the United States took 1371 tons of the 2338 tons, while the United Kingdom took 346 tons, Canada 572 tons, and Australia 49 tons.

Of late quite large quantities of kauri gum have been going forward to the United States as shipping space could be obtained, and there are still large quantities in hand here for export, and it would seem there would be no difficulty in getting all of the kauri gum necessary from now on.—*American Journal of Pharmacy*, June, 1920.

CALCIUM.*

COMPARISON OF TEN DIFFERENT METHODS OF ESTIMATION.

By GEORGE E. ÉWE

Standard Material.—Practically white, doubly refractive calcite.

Preparation of Standard Material for Analysis.—The calcite was ground to a fine powder in an agate mortar, dried to constant weight in a platinum dish over a flame which was not permitted to touch the dish. The dried calcite was free from caustic as shown by its failure to turn red litmus-paper when 1 gm. was made into a paste with a little water and tested with litmus-paper. The dried calcite was preserved in a glass stoppered weighing bottle.

Impurities in the Standard Calcite.—The usual impurities of calcite are silica, ferric, aluminium, magnesium, and manganese compounds.

The standard calcite yielded the following proportions of these impurities:

SiO ₂	0.0119	
			0.0123	Av., 0.0121 per cent.
Fe ₂ O ₃ , Al ₂ O ₃	0.01319	
			0.01360	Av., 0.0134 per cent.
MgO	None
Manganese	None

Silica.

A 0.5 gm. sample was weighed in a platinum dish, a very little water was added followed by 5 cc. hydrochloric acid (1 : 1). The mixture was evaporated to dryness and the residue baked at 200° C. until free from the odour of the acid; 20 cc. of 1 : 1 hydrochloric acid was then added and

the mixture boiled for about 10 minutes; 30 cc. water was added; the mixture was boiled and the silica collected on a filter and washed well with hot water. The filtrate was put through the same procedure again but only an unweighable amount of silica was obtained. The filter containing the silica was ignited to constant weight over a blast lamp and weighed; the weight of the silica being corrected for the ash of the filter.

Ferric and Aluminium Oxides.

The filtrate from the silica was made alkaline with freshly distilled ammonia, only a slight excess of ammonia being used; a few drops of bromine water was added and the mixture boiled until only a very faint odour of ammonia was perceptible. The oxides were filtered off, redissolved in hot dilute nitric acid and reprecipitated with ammonia as before; they were then filtered off, washed thoroughly with hot water and ignited over the blast a short time to constant weight.

The weight of the combined oxides was then corrected for the filter ash.

Magnesia.

The filtrate from the ferric and aluminium oxides was rendered alkaline with ammonia, boiled, and 20 cc. of boiling saturated solution of ammonium oxalate added. The mixture was boiled for five minutes and allowed to settle. The calcium oxalate was filtered off and washed with hot water several times, redissolved in dilute hydrochloric acid and reprecipitated as before. The filtrates from the two precipitations of calcium oxalate were acidified and evaporated to about 150 cc.; cooled and treated with 17 cc. of 28 per cent ammonia water, followed by 15 cc. of a 10 per cent sodium phosphate solution. The solution was stirred well and allowed to stand over night. No weighable amount of precipitate could be obtained.

Manganese.

Volhard's reaction (a solution of 0.5 gm. of the calcite in 5 cc. concn. nitric acid was boiled with an excess of lead peroxide, then diluted with 25 cc. of water and the insoluble matter allowed to settle), yielded no trace of violet-red colour, therefore it was concluded that no more than a negligible proportion of manganese was present, if any.

Theoretical CaCO₃ Content of Standard Material.

No evidence was obtained as to how the Fe₂O₃ and Al₂O₃ were combined in the calcite, but it was arbitrarily taken that the two oxides were present in equal proportions and combined as carbonates in the "ic" state, since the proportions were too small to exert any but a negligible influence on the calcium determinations.

Likewise the state of combination of the SiO₂ was not determined, and while it may have been present in some form of combination with calcium, yet the amount concerned would be negligible, and as a consequence the SiO₂ was arbitrarily considered as being present in the free state.

Per Cent.

The proportion of silica (SiO ₂) was ...	0.0121
The proportion of Fe ₂ O ₃ plus Al ₂ O ₃ was 0.0134 per cent, which, figured to the carbonate state, amounted to ...	0.0286

The total of impurities, therefore, was 0.0407

The difference between this figure (0.0407 per cent) and 100 per cent was considered to represent

* From Bulletin of the International Metallurgical and Chemical Society.

the CaCO_3 content of the standard material. Thus, the CaCO_3 content was theoretically 99.959 per cent.

Details of the Different Methods of Estimation of Calcium.

No. 1. Precipitating as calcium oxalate and weighing as calcium carbonate.

A 0.5 grm. sample was freed from silica and iron and aluminium by the methods mentioned under "Methods of Determining Impurities." The calcium was precipitated as oxalate as mentioned under "Methods of Determining Impurities," except that it was washed more thoroughly. The calcium oxalate was dried on the filter, ignited in a platinum crucible separate from the filter to a faint redness for fifteen minutes in order to convert all of the oxalate to carbonate. This ignition may result in the formation of a little calcium oxide, so, after weighing, the contents of the crucible were moistened with water and a small lump of ammonium carbonate added; the ammonium carbonate was driven off by heating the crucible on a water-bath and the crucible then ignited to a very faint redness. This treatment was repeated until constant weight was obtained and the contents of the crucible no longer turned red litmus-paper.

Results No. 1—99.64

2—99.49 Av., 99.57 per cent CaCO_3

No. 2. Precipitating as calcium carbonate and weighing as such.

A 0.5 grm. sample was freed from silica and iron and aluminium oxides by the methods outlined under "Methods of Determining Impurities." The filtrate from the iron and aluminium oxides was treated with a little ammonia water and then ammonium carbonate solution in slight excess was added. The precipitated calcium carbonate was allowed to settle for several hours on the top of a covered hot water-bath; it was then filtered off and washed with water containing a little ammonia; dried and ignited separate from the filter and weighed as calcium carbonate as described under Method No. 1.

Results ... No. 1—100.05

2—100.10 Av., 100.07 per cent.

No. 3. Liberating CO_2 by means of hydrochloric acid and weighing the liberated CO_2 in KOH solution.

The calcite was placed in an Erlenmeyer containing a three hole rubber stopper. Through one of the holes a glass tube was placed. This glass tube extended to the bottom of the Erlenmeyer. The other end of the tube was connected with several potash bulbs to prevent access of the CO_2 of the air into the Erlenmeyer. The second hole of the rubber stopper contained a glass tube which reached just below the stopper. The other end of the tube was connected first with a calcium chloride tube, then with a bulb containing sulphuric acid, then with a weighed potash bulb followed by a weighed soda-lime tube which was guarded from the air by an unweighed soda-lime tube. The third hole in the stopper of the Erlenmeyer contained a separatory funnel containing about twice the quantity of recently boiled 10 per cent hydrochloric acid theoretically required to liberate all of the CO_2 from the sample of calcite.

The assay was made as follows:—Air was drawn for about 15 minutes through the apparatus

by means of an aspirator attached to the soda-lime guard tube, thus the air entered the train of potash bulbs and was depleted of CO_2 ; it then entered the Erlenmeyer containing the sample and then in turn the calcium chloride tube and sulphuric acid bulb which depleted it of moisture. The air then entered the weighed potash bulb, from which it took up some moisture and which it then deposited in the weighed soda-lime tube which was guarded against the moisture and the CO_2 of the air and aspirator, by the unweighed soda-lime tube at the end of the train. The weights of the weighed potash bulb and soda-lime were then obtained and any variation from their previous weights was noted. The weighed potash bulb and soda-lime tube were replaced in the train, the current of the air was re-established and the 10 per cent hydrochloric acid in the separatory funnel was allowed to drip into the Erlenmeyer, where it came into contact with the calcite and liberated CO_2 , which was dried by passing through the calcium chloride tube and sulphuric acid bulb and then caught by the weighed potash bulb and soda-lime tube. The air was allowed to pass for 15 minutes, during which time the contents of the Erlenmeyer were stirred up by the current of air and warmed a trifle by external heat. The weighed potash bulb and soda-lime tube were then allowed to stand in the balance case for about 15 minutes and weighed. When not connected in the train, the ends of the weighed potash bulb and soda-lime tube were kept closed by small rubber nipples, which were removed momentarily and then replaced before each weighing in order to insure absence of pressure or vacuum within the bulb and tube. The increase in weight of the potash bulb and tube corrected as found necessary by the blank was considered to be due to the CO_2 from the calcite and was calculated into terms of CaCO_3 .

Results No. 1—99.57

2—100.50 Av., 100.03 per cent CaCO_3

No. 4. Precipitating as calcium oxalate and weighing as calcium oxide.

In all respects this method was similar to No. 1 with the exception that the calcium oxalate after gentle ignition was made into a paste with water and spread around the sides of the crucible so that the calcium oxide would be obtained in a very thin layer. This was found essential because of the tenacity with which calcium carbonate retains its carbon dioxide. Finally the crucible and its contents were ignited to constant weight before a blast lamp and the weight was corrected for the filter ash.

Results ... No. 1—99.75

2—99.98 Av., 99.86 per cent.

No. 5. Precipitating as calcium sulphate and weighing as such.

0.5 grm. of the calcite was freed from silica and iron and aluminium oxides as mentioned under "Methods of Determining Impurities." The filtrate from the iron and aluminium oxides was treated with a slight excess of dilute sulphuric acid and the solution was diluted with twice its volume of alcohol. The precipitate of calcium sulphate was allowed to settle over night, filtered off, washed thoroughly with alcohol, dried and ignited separately from the filter, using only a

cherry-red heat for ignition. The weight of ignited CaSO_4 was then corrected for filter ash and calculated to CaCO_3 .

Results ... No. 1—99.64
2—99.73 Av., 99.68 per cent.

No. 6. Precipitating as calcium oxalate and weighing as calcium sulphate.

A 0.5 grm. sample of the calcite was treated as in Method No. 1 to obtain the calcium oxalate which was then separated from the filter. The filter was ignited and the calcium oxalate was then placed in the crucible. A little 10 per cent sulphuric acid was then added to the contents of the crucible, which was then thoroughly dried on a water-bath and very carefully ignited with the cover on, gradually increasing the heat until a cherry-red heat was attained. The crucible and contents were then weighed. The treatment with sulphuric acid was repeated until constant weight was obtained upon subsequent weighings.

Results ... No. 1—100.15
2—100.64 Av., 100.39 per cent.

No. 7. Precipitating as calcium oxalate and titrating with potassium permanganate.

The sample of calcite was treated as in Method No. 1 to obtain the calcium oxalate which was filtered off, washed with hot water until free from soluble oxalate, transferred to the beaker in which it was precipitated by spreading the filter paper against the side of the beaker and washing down the precipitate first with hot water and then with dilute sulphuric acid (25 per cent); reserving the washed filter by hanging it across the edge of the beaker; 50 cc. of water was then added followed by 10 cc. of concentrated sulphuric acid; the solution was heated just to boiling and then titrated to the first pink change with 0.1/N potassium permanganate; then the filter paper was dropped in, causing the pink colour to be discharged owing to the trace of oxalate still present in the paper, and finally the end point was obtained by a few drops of the 0.1/N potassium permanganate. The permanganate was standardised against calcium carbonate obtained from the standard calcite as in Method No. 2. This calcium carbonate was considered as being 100 per cent CaCO_3 . The method of standardisation was as follows:—

A weighed portion of the freshly ignited CaCO_3 (free from CaO) was dissolved in hydrochloric acid and precipitated as calcium oxalate as mentioned under "Methods of Determining Impurities," and this calcium oxalate was dissolved in sulphuric acid (25 per cent) and hot water as mentioned a few lines above and the permanganate solution run in to the end point, including the few additional drops required by adding the washed filter upon which the oxalate was collected to the titrated liquid.

Results ... No. 1—99.91
2—99.46
3—99.90
4—99.47 Av., 99.68 per cent.

No. 8. Precipitated as calcium oxalate from a slightly acid solution.

0.5 grm. sample of the calcite was dissolved directly in dilute hydrochloric acid; the solution was diluted to 150 cc. and made barely alkaline with freshly distilled ammonia; a hazy precipitate of ferric and aluminium hydroxides resulted;

hydrochloric acid was added drop by drop until acid, then 2 drops in excess was added. The mixture was then boiled and the calcium totally precipitated as calcium oxalate by means of an excess of ammonium oxalate solution. The precipitated calcium oxalate was allowed to settle and was then filtered off and titrated with 0.1/N potassium permanganate as in Method No. 7.

Result ... 99.82 per cent CaCO_3 .

The experiment was repeated using acetic acid to dissolve the calcite and adding 2 drops of acetic acid in excess before precipitating with ammonium oxalate.

Result... 99.91 per cent CaCO_3 .

Discussion of Method No. 8. The results obtained by this method indicate that calcium can be precipitated quantitatively as oxalate from a slightly acid solution. The acidity of the solution is due solely to the presence of oxalic acid which is liberated by the slight excess of hydrochloric acid or acetic acid present in the solution. This fact is made use of by Meade for the rapid determination of calcium in cement without previous separation of silica and ferric and aluminium oxides. The method described by Meade is essentially as described above with the following exceptions: The acid solution of the cement is rendered just alkaline with ammonia and then 10 cc. of a 10 per cent solution of oxalic acid is added to render the mixture acid and redissolve the hydroxides of iron and aluminium which are partially precipitated when the mixture is rendered alkaline with ammonia. In order to test the value of Meade's method a sample of limestone yielding the following analysis by Method No. 7 was employed as a standard:—

SiO_2	3.320	
	3.300	Av., 3.310 per cent
$\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3$	1.030	Dup., 1.030 per cent
CaCO_3	77.130	
	77.125	Av., 77.127 per cent
MgCO_3	18.377	
	18.332	Av., 18.355 per cent

Total 99.822 per cent

Meade's method was applied in detail to a sample of this limestone with the one exception that the calcium oxalate was finally weighed as calcium sulphate according to Method No. 6, instead of being titrated by permanganate as required in Meade's Method. The yield of CaCO_3 was 77.18 per cent. Another assay was made using acetic acid to dissolve the limestone and a yield of 77.31 per cent CaCO_3 was obtained.

No. 9. Liberation of CO_2 by dilute hydrochloric acid and calculating loss of CO_2 into terms of CaCO_3 .

The apparatus known as "Geissler's new form carbonic acid determination apparatus," listed on page 103 of the catalogue of Eimer and Amend, New York, was employed.

The method consists of treating a weighed sample of the calcite in the apparatus with dilute hydrochloric acid and drawing the liberated CO_2 through the sulphuric acid compartment of the apparatus; the entrance and exit of the apparatus being properly guarded by bulbs containing concentrated sulphuric acid.

Results ... 99.68
99.93 Av., 99.80 per cent CaCO_3 .

No. 10. Residual titration method.

A 0.5 grm. sample of the calcite was placed in a flask connected with a straight tube reflux condenser. A measured excess of 0.2/N H_2SO_4 was run into the flask. The flask was connected with the reflux condenser and heated by a flame until the reaction was complete. The condenser was then washed with water, allowing the washings to flow down into the flask and the excess of 0.2/N H_2SO_4 was titrated with 0.1/N Na_2CO_3 , using methyl orange as indicator. The 0.1/N Na_2CO_3 was standardised by accurately weighing out the proper quantity of freshly ignited, chemically pure sodium carbonate and the 0.2/N H_2SO_4 was standardised against the 0.1/N Na_2CO_3 .

Results ... 99.66
99.83 Av., 99.75 per cent CaCO_3

For convenient comparison the results are here-with presented in tabular form:

Theoretical CaCO_3 content of standard material, 99.959 per cent.

No.	Method.	CaCO_3 found. Av. per cent.
1—	Precipitating as calcium oxalate and weighing as calcium carbide ...	99.64 99.57
2—	Precipitating as calcium carbonate and weighing as such ...	100.05 100.10 100.07
3—	Liberating CO_2 with HCl and weighing liberated CO_2 in KOH solution	99.57 100.50 100.03
4—	Precipitating as calcium oxalate and weighing as calcium oxide ...	99.75 99.98 99.86
5—	Precipitating as calcium sulphate and weighing as such ...	99.64 99.73 99.68
6—	Precipitating as calcium oxalate and weighing as calcium sulphate ...	100.15 100.64 100.39
7—	Precipitating as calcium oxalate and titrating with potassium permanganate ...	99.91 99.46 99.90 99.47 99.68
8—	Precipitating as calcium oxalate from a slightly acid solution ...	99.82 99.91 99.87
9—	Liberation of CO_2 by HCl and calculating loss of CO_2 into terms of CaCO_3 ...	99.68 99.93 99.80
10—	Residual titration method	99.66 99.83 99.75

RUSSIA'S CONTRIBUTION TO SCIENCE.*

By ALEXANDER PETRUNKEVITCH, Ph.D.

(Continued from p. 41).

He took interest in local affairs and was a member of the Luga County Zemstvo and of the St. Petersburg Zemstvo. Although very exacting to his students in the laboratory, he was a friend of all who were striving to acquire education and was for many years president of a committee of aid to needy students.

It seems to be scarcely necessary to review the work of the greatest of all Russian chemists and the pride of all to whom Russia means more than a land of mystery, surprises, Kazaks, knuts, vodka, and revolution. But the account would be incomplete without some reference to Dmitri Ivanovitch Mendeleeff, the creator of the periodic system. He was born in 1834 in Tobolsk in Siberia, the youngest of a family of seventeen. His father died while he was a child and his mother when he was a youth of fifteen. At first he attended a gymnasium in Tobolsk, then in Moscow. Later he studied at the Pedagogical Institute of St. Petersburg and the St. Petersburg University. As a student he published his first research in chemistry concerning isomerism. After graduation he became a high school teacher first in Sympheropol then in Odessa. Only in 1856 had he been appointed Privatdozent in chemistry at the University of St. Petersburg, after the successful public defence of his dissertation on the subject of "Specific Volumes." In 1859 he went to Heidelberg, where he made a research in capillarity of fluids. While there he also began the publication in Russian of his course in organic chemistry. In 1863 he returned to Russia and was appointed professor at the Imperial Technological Institute. At this time questions of applied chemistry and technology occupied most of his attention. He investigated the oilfields of Baku in the Caucasus and performed various experiments in connection with agricultural problems. In 1866 he was appointed professor of chemistry at the University of Petrograd. In 1868 he began the publication of his principles of Chemistry, wherein he propounded for the first time his periodic law. This work marked an epoch in the study of chemistry and was repeatedly reprinted with additions and corrections made by the author. It was also translated into many languages and brought him later in 1882 as reward for his discovery the Davy medal of the Royal Society. The arrangement of the elements into short and long periods according to their atomic weight and properties showed the presence of various gaps in the series and permitted Mendeleeff to predict the existence of the yet unknown, missing elements as well as their atomic weight and properties. This prediction is justly likened to the prediction of the planet Neptune by Leverrier from his mathematical calculations. And indeed two years after the prediction in 1871, the first element was discovered, and called gallium (Mendeleeff proposed the name ekaboron). In 1879 was discovered scandium (Mendeleeff's ekaaluminium) and in 1886 germanium (Mendeleeff's ekasilicon). In several cases Mendeleeff ventured to question the correctness

* From the Transactions of the Connecticut Academy of Arts and Sciences, June, 1920.

of the commonly accepted atomic weights, because they did not fit rightly into his periodic system, and later investigations proved the correctness of his assertion. In 1888 he made an exhaustive study of the Donetz anthracite industry and was subsequently appointed member of the council of trade and manufacture. To this period belongs also his work on smokeless powder done at the request of the ministry of war. In 1893 he resigned his professorship to become Director of the Bureau of Weights and Measures. In 1902 in a paper on the chemical conception of ether he gave expression to a hypothesis that ether is a gaseous element with an atomic weight smaller than that of hydrogen. Mendelejeff died in 1907 and the list of his works comprises over 140 titles including many investigations in various branches of physical chemistry, such as indefinite solutions, expansion of liquids with heat, &c.

But for lack of space it would be unjust to pass in silence over the splendid work done by Russian chemists in recent years. I cannot refrain however from mentioning V. N. Ipatiev's extensive researches in organic chemistry, especially in hydrogenation of oils; and I. I. Ostromuiskii's investigations of rubber.

In the closely interrelated sciences of crystallography, mineralogy, petrography, and physical geology, several names stand out amidst a number of less known investigators. Ewgraf Stepanovich Fedoroff was the first to prove that all crystals belong to the one or the other of the 32 possible types of symmetry and created the nomenclature afterwards accepted by Grote and others. He was a productive worker and made many researches in geometry, crystallography, geology, physical and descriptive, ores, &c.

His pupil and my teacher in crystallography and mineralogy, Wladimir Ivanovitch Vernadsky, one of the broadest and best educated men in the world, is the real creator of the mineralogical museum in Moscow and author of many researches. He investigated the mines of Austria and Germany in 1894 during which trip I had the privilege of accompanying him and shall never forget his enthusiasm, energy and perseverance. He worked at that time from morning till late in the evening, collecting minerals, visiting mines, museums, art galleries and points of interest and in the evening when I was totally exhausted and ready to fall asleep, he would open some new treatise on history of art, or civilisation or sociology and read until late into the night. Later he took part in the liberating movement of Russia, was member of the Imperial Council, and quite recently member of the Provisional Government, remaining in Petrograd at his post when the Kerensky Government was fighting its last battle. A man of the tenderest heart, a friend of youth, he lived through most trying experiences during the student revolt, enduring discomforts and incurring insult for extending with fatherly love his protection to persecuted students.

Alexander Alexandrovitch Inostranzen was perhaps the most distinguished Russian geologist, born in 1843. He travelled a great deal throughout European Russia, the Caucasus, and the Ural mountains and published many works, among which I cannot omit mentioning his two volumes of Materials for the Geology of Russia, published in 1869, his

Geological Investigations of the North of Russia, published in 1872, his sub-division of the stone age into periods, published in 1880, and his Treatise of Geology, published in 1885 and reprinted several times with additions and revisions. Inostranzen was for years president of the geological section of the St. Petersburg Society of Naturalists and president of the Russian Anthropological Society. He worked up the geological collection brought by Przewalsky, Potanin, Pievtzov, and others, and made the St. Petersburg Geological Museum one of the best in Russia. It may be interesting to recall to memory the fact that the Philadelphia Academy of Sciences elected Inostranzen corresponding member.

One more name should be mentioned in connection with geological and mineralogical sciences. It is the distinguished name of the unfortunate Dokutchaeff, who did so much for the elucidation of the nature of the black earth in Russia, created a school of learning, founded a museum of natural science in Poltava and another in Nishnij Novgorod, and succumbed finally to a slow affection of the brain. He described the formation of the river valleys in European Russia in 1878, and in the next year gave expression to the then novel idea of the influence of the geographical factor in the formation of soils. In 1883 in his standard work on Russian black earth he explained its origin through the decomposition of the herbageous plants of the steppe under the influence of climatic factors which exist even at present. He published many investigations on soils which he regarded as things different from minerals and rocks and the study of which he raised to the level of a separate science. His private life, full of privations, sufferings, disappointments, and struggle, is one of the saddest chapters in the history of Russian men of science and will be for ever an example of achievement through nothing but talent and indomitable will.

Turning our attention to biological sciences in the broader sense of the word, I should like to touch only briefly on physiology and adjoining fields of knowledge, for this science is so intricately connected with other aspects of human life that it should find special consideration in connection with medicine. Four names command our admiration, Setchenoff, Tarkhanoff, Pavloff, and Bekhtereff, each with a group of followers many of whom are known throughout the world.

Ivan Mikhailovitch Setchenoff, born in 1829, received his first education as officer in a military academy, but left service to study medicine at the University of Moscow from which he graduated in 1856. He occupied the chair of physiology at first at the Medico-Surgical Academy, then at the Novorossiisk University, then at the University of St. Petersburg, and finally at the University of Moscow, where he served until he was retired, continuing in the capacity of private-doctor and emiritus at the same time. He was a man of broad knowledge and deep thought, commanding the respect and admiration of the widest circles. He published investigations about the gases in the blood, about alcoholic intoxication, cerebrospinal reflexes, about centres inhibiting reflexes, about the innervation of the heart, and so on. Especially well known in Russia are his "Physiology of Vegetative Processes," "Reflexes of the Brain," "Psychological Studies," and "Elements of

Thought." I remember his speech at the meeting of physicians and naturalists in Moscow more than 25 years ago on the subject of "What is Thought?" Unassuming and quiet, he spoke in the immense assembly hall of the Moscow nobility without raising his voice, which nevertheless was heard by everybody in the audience.

Prince Ivan Romanovitch Tarkhan Mouravov, better known as Tarkhanoff, a Georgian by nationality, born in 1846, was for many years professor of physiology at the Medical Academy of St. Petersburg. His works embrace the physiology of thermic reflexes, the innervation of the spleen, the application of the telephone to the study of animal electricity, the physiology of the normal sleep in animals, the automatic movements of decapitated animals, the influence of music on animals and man, &c.

The physiologist best known in foreign countries, and one of the most remarkable experimenters of the world is Ivan Petrovitch Pavlov, born in 1849, and professor of physiology at the Medical Academy of St. Petersburg since 1890. His investigations extending over many years and contained in numerous articles may be divided into three groups: work relating to the innervation of the heart, work in connection with the so-called Eck fistula, and work on the secreting activity of the stomach. In the first series of papers, Pavlov has shown that besides centres accelerating and retarding the heartbeat, the heart possesses also centres augmenting and depressing the strength of the heart-beat. In the second series of experiments Pavlov used the operation suggested by his teacher Eck and consisting in an artificial connection of the portal vein with the inferior caval vein. Through this connection the blood flowing from the digestive organs was diverted from the liver and the function of the latter organ can be studied independently. It was thus that Pavlov was enabled to show how the liver acts as an organ absorbing from the blood harmful substances and purifying it.

But the most celebrated of his investigations are those based on œsophagotomy, *i.e.*, on an operation consisting in the severing of the œsophagus and the production of an artificial fistula, allowing a direct observation of the contents of the stomach under various conditions. This operation is too well known to require an explanation or detailed description here. The results of these investigations, which have been translated into many languages, may be briefly summarised as follows: the secretion of saliva is caused by reflexes through smell, sight, &c., before food is taken into the mouth. Similarly the secretion of the gastric juice is induced by a psychic condition before food is taken into the mouth. If, unknown to the animal, solid food is introduced directly into the stomach through the fistula, no secretion of gastric juice takes place for at least an hour. Mechanical stimulation is ineffective.

Studying the chemical phenomena of digestion Pavlov used another remarkable operation consisting in the artificial production of an accessory miniature stomach connected with, yet separate from the main one. The action of the vagus nerve which conveys the excitation to the glands of the stomach was excluded by a division of this nerve. Thus Pavlov was able to show that meat

juice and beef extract cause secretion while no secretion of gastric juice follows the introduction of eggwhite, fat, or starch into the stomach.

Wladimir Mikhailovitch Bekhterev, born in 1857, is an alienist by profession. As such, he has had a great deal to do with normal and pathological functions of the nervous system. His works embrace a wide range of subjects from the anatomy of the nervous system to the psychopathy and its relation to responsibility before the law. He wrote on the physiology of the central nervous system, especially on the localisation of tactile and pain centres in the brain. In 1884 he published an interesting paper on the formation of our conception of space. Induced by special circumstances he has also made a psychological and ethnographical investigation of the semi-barbaric Votyaks and published a paper on their history and present status.

Many were the Russian workers in botany and there is scarcely a branch of this science that has not been made subject of thorough investigation. Nicolai Ivanovitch Annenkov, born in 1819, was the first student of the local flora. To his patient work in this field is due our knowledge of it. He prepared the celebrated herbarium kept in the botanical Museum of Moscow University. He wrote the "Flora Mosquensis Exsiccata," and later in 1859, the "Botanical Dictionary," which is a most valuable reference book. His successor in the field of systematics was Nicolai Nicolaevitch Kaufmann, born in 1834, whose "Moscow Flora" reprinted many times plays in Russia the rôle of Gray's Manual and is in the hands of every student of flowering plants. Lev Semenovitch Cienkowski, born in 1822 in Warsaw, was the most distinguished student of the lowest plant organisms of his day. In his paper on "The Lowest Algæ and Infusoria," published in 1856, he was the first to express the idea that these organisms are not complicated creatures as taught by Ehrenberg, but unicellular forms. His earlier works are mostly on myxomycetæ, fungi, and algæ. Later he was particularly interested in Bacteriology and shares with Pasteur the distinction of founder of this science. He applied his knowledge also to practical ends and has described an improved method of inoculation against anthrax.

(To be continued).

NOTICES OF BOOKS.

Animal and Vegetable Oils, Fats, and Waxes.

By GEOFFREY MARTIN, D.Sc. (Lond. and Bristol), Ph.D., F.I.C. Pp. x+205. London: Crosby Lockwood & Son, 7, Stationers' Hall Court, E.C.4. 1920.

THIS book represents the ninth manual belonging to the series known as the "Manuals of Chemical Technology." The volume includes the extraction, refining, and analysis of animal and vegetable oils.

During the last few years, very great changes have been made in the oil industry. To quote two examples—(1) that of the recovery of oil from waste materials of all kinds, and (2) the hydrogenation of fats. The latter subject is dealt very fully by Dr. Martin in Chapter ix., and his explanations

are interspersed with many illustrations of machinery both diagrammatic and photographic.

The author has separated his text into two parts, the first half of the book giving the methods of extraction and refining of oils, and the latter half is given up to the chemistry of oils, fats, and waxes, included in which are the constants for certain of the oils which are met with in everyday life and the methods of analysis of fatty oils, including butter and margarine.

At the end of Chapter x. is given a summary of the chemical and physical properties of the better-known oils.

In two appendices are given (1) the Report by a Committee of Analysts on Standards for Oil of "Good Merchantable Quality," and (2) a Report on Standard Methods of Analysis of Seeds, Nuts, and Kernels, Fats and Oils, and Fatty Residues.

For those anyway interested in the technology of oils, this book can well be recommended, and the reader may supplement his knowledge gained from the book by means of a copious bibliography which is given at the commencement of every chapter.

CORRESPONDENCE.

ISOTOPIC B, Si, Br, & S (?). NON-ISOTOPIC F, As, & P (?).

To the Editor of the Chemical News.

SIR,—Dr. Aston, in *Nature* of July 1, 1920, reports the discovery of further isotopes with masses as follows:—

Boron ...	10 and 11.
Silicon...	28 and 29 (and 30?).
Sulphur ...	32 (and one other?).
Bromine ...	79 and 81; approx. equal parts.

In addition, non-isotopic masses are recorded corresponding with:—

Fluorine ...	19	These are exact whole-number masses without measurable fractions.
Phosphorus ...	31	
Arsenic ...	75	

The question might now be raised: Why are there so many cases of odd-and-even-number atomic weights which correspond respectively with odd and even valencies? (See H. Collins, *CHEMICAL NEWS*, 1907, xcvi., p. 176, and later papers for observations in this connection.)

Referring to the scheme shown on p. 183 of this *Journal* of April 16 last (vol. cxx.), there are no exceptions to this regularity apart from nickel, cobalt, and nitrogen (non-isotopic). In the cases of the boron isotope 10 (my value was 9) and the silicon isotope 29 (my value was 30) the odd-and-even rule appears to be violated.

If, however, hydrides are involved, this difficulty in securing greater harmony might be accounted for. It must be remembered that of all the elements so far analysed by Aston, they are those which readily form hydrides except the inert gases and perhaps mercury (see *CHEMICAL NEWS*, cxx., p. 205, third par., and cxxi., p. 2).

The values I suggested for bromine (*CHEMICAL NEWS*, cxi., January 8, 1915, p. 13) were 79 and 80.

In this connection, the redetermination of the atomic weight of silicon by Baxter (*Journ. Am. Chem. Soc.*, June, 1920) is of interest because the value reduces from 28.3 (present value) to 28.1.

A mean figure would be 28.2, which should be taken, in my opinion, until the experimental value can be regarded as closely accurate in the second decimal place.—I am, &c.,

F. H. LORING.

THE STRUCTURE OF MATTER.

To the Editor of the Chemical News.

SIR,—In the *CHEMICAL NEWS* of April 16th this year Mr. Loring says, "Let it be assumed that when isotopes occur in the process of evolution, their number is proportional to the masses of the outriders." Later he says, "In evaluating the proportionate numbers of isotopes I have cubed the mass of the outriders." The effect of this can be best illustrated by examples. In the case of lithium he has obtained 6.93 by taking the average of 27 sevens and one five, which is of course just below 7. If the at. wt. of lithium had been just above 7 instead of below, it seems that Mr. Loring would have found the average of 27 sevens and one nine.

In the case of silicon he finds the average of 64 twenty-eights and 8 thirties.

It is evident that the large multipliers 64 and 27 entirely swamp the arbitrary numbers taken for the isotopes of the elements.

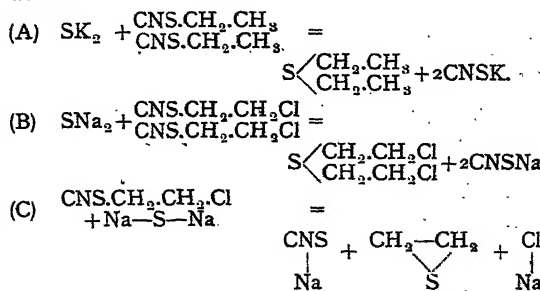
Mr. Loring's deductions lead up to the following question: Why should the number of each proposed isotope be proportional to the cubes of the masses of portions of these hypothetical isotopes?

In every case the mean at. wt. will be just above or just below the nearest whole number according as he chooses the isotopes.—I am, &c.,

HAWKSWORTH COLLINS.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxxi., No. 1, p. 36. ETHYLENE SULPHIDE.—M. Marcel Delépine.—The author gives a method for the production of ethylene sulphide the simplest of the cyclic series first prepared by Grichkévitich-Trokhimovsky in 1916 (*Journ. Soc. phys. chim. russe*, 1916, xlviii., p. 880). He makes use of the following reactions:—



The properties of this substance are given; it is described as a colourless liquid of very strong odour, insoluble in water, but soluble in the usual organic solvents; it boils at 55°-56°; density at 0/4° = 1.0368.

NOTES.

THE PROFITEERING ACTS: CENTRAL COMMITTEE.—At the invitation of the President of the Board of Trade, Mr. John Murray, M.P., has accepted the appointment of Chairman of the Central Committee under the Profiteering Acts, in succession to the Rt. Hon. C. A. McCurdy, K.C., M.P., whose duties as Food Controller do not enable him to spare the time to continue to act as Chairman of the Committee.

THE PHYSICS AND CHEMISTRY OF COLLOIDS AND THEIR BEARING ON INDUSTRIAL QUESTIONS.—The Faraday Society and the Physical Society of London are arranging to have a joint Symposium and General Discussion on this important subject next October. The subject will be introduced by a brief survey of the present position of colloidal physics and chemistry and discussion will then follow on the following sub-divisions of the subject: Emulsions and Emulsification; Physical Properties of Elastic Gels; Cataphoresis and Electro-endosmose; Precipitation in Disperse Systems; Glass and Pyrosols; Non-Aqueous Systems. In spite of the importance of colloidal physics and chemistry in many branches of manufacture and of the interest which the subject has aroused in recent years, much light remains to be thrown on the nature of the manufacturing process in which colloids play a part. It is hoped that the discussion will focus attention on some of these problems and that its result will be to indicate lines of advance and suggest further researches, and that it will be fruitful not only in helping to a fuller understanding of the laws of the colloidal state but also in suggesting new applications for colloids in the laboratory and in the works. The exact date and place of meeting and further particulars will be announced later. In the meantime anyone desirous of using the opportunity of the discussion to bring forward experimental matter or theoretical considerations bearing on the above-mentioned branches of the subject is asked to communicate as soon as possible with the Secretary of the Joint Committee, Mr. F. S. SPIERS, 10, Essex Street, London, W.C.2.

NOTICE.

OWING to the greatly increased cost of printing and paper, and the advance in the postal rates, we have been compelled to raise the price of the **CHEMICAL NEWS** from 4d. to 6d. (by post 7d.). The new subscription rates are as follows:—

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3147.

EDITORIAL.

A CIRCULAR has been issued by the British Chemical Ware Manufacturers' Association urging upon Members of Parliament the need to hasten and support the Key Industries Bill that, amongst other things, will safeguard the manufacturers of chemical ware against undue foreign competition during the development of manufactures, that before the war were practically non-existent in this country. Since 1914 many makers of glass and porcelain ware, although faced with the risk of considerable pecuniary loss, turned their attention to the production of apparatus that had hitherto a Central Europe monopoly. Costly experiments have been carried out and great progress has been made, material has been produced, equal, and in many cases superior to that of pre-war foreign supply. The chief difficulty is that of training labour to produce the special apparatus needed; this of necessity will take time, but the production is rapidly increasing. The demand is so great, that large extension and development of factories is necessary and considerable financial risk has yet to be incurred. Manufacturers feel that if they can be secured against the dumping into this country of foreign made goods during the period necessary to establish the manufacture upon a sound economical basis, the situation that, in the autumn of 1914 imperilled our national existence need not occur again, and a new and lucrative industry will be established at home. We realise that so far a great deal of the British chemical ware that has been produced leaves much to be desired, but users of apparatus must remember that the industry has in many cases been created since 1914, and a little generous patience will go a long way to smooth the difficulties that manufacturers have to contend with. The firm establishment of these Key Industries in our own hands is of supreme importance, and we sincerely hope that our legislators will be able to introduce the measure of support needed in this critical period and so defeat the efforts that are already being made to re-introduce the undesirable conditions that existed before the war.

The following paper has been received for publication, and will be inserted as space permits:—

"Isotopism." By J. Frederick Corrigan. A comprehensive review of theory of Isotopes, with special reference to the bearing of the ideas of Sir William Crookes regarding the existence of Meta-Elements upon the subject, the work of Ashton on Neon, and Sir J. J. Thomson's method of "positive ray analysis."

THE FRUIT OF THE JAPANESE BARBERRY.

By O'NEAL MASON.

THE fruit of Japanese barberry (*Berberis Thunbergii*) was grown on the campus of Cornell College as a part of the ornamental shrubbery. It was gathered in the autumn of 1919, and dried in an oven at a moderate temperature. It consists of small red berries.

The Sugars.—A hundred grms. of the dried fruit was taken for the sugar extraction. It was placed in a half litre flask, fitted with an inverted condenser, and treated with successive portions of 95 per cent alcohol for thirty-five days. The alcohol extraction was removed when the colour became dark, and fresh alcohol applied.

When the alcohol was distilled off, two substances remained: One a dark thick syrup, and the other a resinous or gummy material with a bluish-grey colour. The alcoholic extraction gives acid reaction to litmus paper. At first the colour and odour resembled new cider, but later it smelled like old cider, and the presence of acetic acid indicated that fermentation had taken place.

A test with Fehling's solution at the end of thirty-five days showed that the sugars were nearly extracted, and distilled water was substituted for the alcohol. The berries now became soft and mushy. We changed the water often as it rapidly became quite highly coloured. Ten days were required to remove the residue of the sugar from the fruit.

The quantity of sugar was determined by Fehling's solution of such a strength that 10 cc. corresponded to 0.05 gm. of sugar. The test was made by taking 1 cc. of the sugar extraction and adding 50 cc. of distilled water. It was heated to boiling point and titrated with Fehling's solution.

To ascertain when the end point was reached, a small portion of the solution was filtered from time to time, always pouring back the filtrate. When the reaction was complete, the solution became a light blue. There was found to be 39.5 grms. of sugar, corresponding to 39.5 per cent of the dried fruit. The loss by fermentation (probably small) was not determined.

The alcohol and water extractions were mixed together and on the water-bath evaporated nearly to dryness, and the odour was like scorched sorghum. The residue was a black thick jelly, possessing the bitter taste of the original fruit. A portion of this residue was purified by heating a water solution several hours on the water-bath with pure bone-black. The solution became much lighter in colour, and was evaporated to dryness for treatment with phenyl-hydrazine. With 0.1 gm. sugar, 0.4 gm. phenyl-hydrazine, and 0.2 gm. sodium acetate, the test pointed to fructose. The cobalt nitrate test also indicated dextrose. The osazone crystals formed, but we were not successful in their analysis. The residue of the fruits, after the sugar extraction, was dried and weighed, and the loss was 56 per cent of the original amount. The berries were shrivelled, black, and hard. This portion was dried for the oil determination.

The Ash.—Four different portions of the dried fruit were ashed in a platinum dish of 100 cc. capacity. From the first portion, iron, aluminium, silica, calcium, and magnesium were determined; from the second portion, sodium and potassium by the J. Lawrence Smith method; from the third portion sulphates, and phosphates from the fourth portion. The analysis showed more sodium than potassium, and the flame test from both the original berry and sugar extractions pointed in the same direction. The results are as follows:—

The ash was found to be 4.6 per cent of the original fruit.

SiO ₂	1.87	per cent of the ash
Fe ₂ O ₃	2.42	" " "
Al ₂ O ₃	2.27	" " "
CaO	0.45	" " "
MgO	8.55	" " "
K ₂ O	7.23	" " "
Na ₂ O	8.40	" " "
SO ₂	18.04	" " "
P ₂ O ₅	15.85	" " "

The total per cent found is 65.08. The remainder is carbon dioxide and organic matter that escaped combustion, as complete oxidation in air was difficult. The portion of the fruit remaining after the sugar and oil extractions was thoroughly dried and 2.84 grms. ashed. There remained only 1.75 per cent of ash, less than half that which was found in the original fruit. In burning this residue, it gave the characteristic odour of coffee and burning leaves.

The Oils.—The dried berries from the sugar extraction weighing 56 grms. were finely ground in a mortar and used for the extraction of the oils. The powder was placed in a 500 cc. flask which was fitted with an inverted condenser and ether applied. Two weeks were required to remove all the oil. The ether was removed by distillation, and the oil had a dirty green appearance due largely to the presence of chlorophyll. It was purified by heating twelve hours in a flask with bone-black and ether, using a perpendicular condenser. The bone-black was filtered off and washed with ether and the ether was allowed to evaporate spontaneously. The resulting oil had the colour of amber and somewhat resembled olive oil in appearance and odour.

The specific gravity of the oil was determined by the Maxwell specific gravity apparatus. Two determinations gave 0.9312 and 0.9299. It could not be solidified in a freezing mixture at -15°, but became semi-solid or a pasty mass. It boils at 148°.

Two saponifications were made by the Koettstorfer method. Saponification was difficult and possible only after prolonged heating. The average result, 235, indicates that the oil is an olein, to which group belongs almond oil, olive oil, and castor oil. It seemed to be homogeneous, as when the oil was placed in a freezing mixture, nothing separated out.

The Acids.—The tests for acids were made with the sugar extractions. Besides acetic acid which resulted from the fermentation of the sugar, there were found citric, malic, and tartaric acids, the last two predominating in amount.

The Proteins.—Some of the original berries were boiled a considerable time in distilled water. When a small amount of this solution was heated

with nitric acid a yellow colour was obtained, showing the presence of albumen, confirmed by its turning red with alkali. When heated in a test-tube at a high temperature, the fumes given off reacted acid to litmus. The nitrogen was determined by the Gunning method. 3.0455 of the fruit gave 0.07188 grm. of nitrogen, equivalent to 2.3 per cent.

To ascertain if the albumen contained sulphur, we treated a solution of lead acetate with caustic soda until the precipitate which formed at first redissolved. A solution obtained from boiling the fruit was added to this, but no precipitate of lead sulphur formed, indicating the absence of sulphur in the albumen.

I desire to express hearty thanks to Dr. N. Knight for his suggestions and assistance in carrying out the work.

Cornell College, Mount Vernon, Iowa,
June 19, 1920.

THE ABSORPTION OF COLOURING MATTERS BY CHARCOAL.

By EDMUND KNECHT.

In a recent paper entitled "The Activation of Wood Charcoal by Heat Treatment," by Philip, Dunnill, and Workman (*J. Chem. Soc.*, 1920, p. 302), the authors give an account of the results obtained by them on the action of prolonged heating of wood charcoal to temperatures of 800°-925° C. on its affinity for methylene blue. This they find to be very considerably increased by the treatment. No analyses of the charcoals are given, nor is there any reference to their specific gravities. Still the authors feel themselves justified in making the following statement—

"Attempts have been made (Glassner and Suida, *Annalen*, 1907, p. 95; Knecht and Hibbert, *J. Soc. Dyers and Col.*, 1916, p. 226) to correlate the activity of a charcoal in decolorising solution with its nitrogen content, but the probability of any such relationship must be regarded as exceedingly small in view of the above figures for a wood charcoal."

Evidently the authors cannot have read our paper carefully, for we never claimed that the nitrogen content of charcoals had any influence on their absorptive power for methylene blue, which we chose for the experiments as a type of a basic colour. It is in fact expressly stated (p. 228) that the percentage of nitrogen does not appear to affect this property. Our contention was that the absorptive power of an animal charcoal for an acid colour like crystal scarlet is (for a given sample) proportional to the amount of fixed nitrogen which that carbon contains, and this contention has not been in any way controverted up to now. It is regrettable that the authors should have made use of such an extreme and definite expression, which is at variance with experimental evidence. I still hold that the absorption of methylene blue is in some way connected with the oxygen content of the charcoal, and until there is definite proof that pure amorphous carbon will act in this way the phenomenon must be attributed to chemical and not to mechanical forces. The acetylene black referred to in

our paper represents a relatively pure form of amorphous carbon as is shown by the analysis and has practically no affinity for methylene blue. (The samples designated, acetylene black II. and III., were obtained by exploding acetylene diluted with carbon dioxide in order to diminish the shock, and as the analyses show, did not represent pure carbon). Having been formed by the explosion of acetylene it must have been exposed in *statu nascendi* to a very high temperature, and possesses an exceptionally low apparent specific gravity. (I am not aware that this has been directly determined, but from thermo-chemical considerations it would appear to be in the vicinity of 2750° C.). These conditions should constitute it from the mechanical point of view an excellent decolorising agent, whereas experience shows that it is practically devoid of this property.—*Journal Soc. Dyers and Colourists*, July, 1920.

THE GENERATION OF LARGE POWERS AT RADIO FREQUENCIES.

THERE was a stage in the development of the low-frequency alternate current generator when the outstanding feature was diversity of design. Armatures were sometimes inside and sometimes outside the field system; the outside member was generally fixed, but in some cases, as at Niagara, the inside member was fixed and the outside member rotated around it. There was the Lauffen type with claw-poles, the Mordey Victoria with a stationary disc armature, the Ferranti with a rotating disc armature and various types of inductor alternators. With time came a gradual elimination and standardisation, modified only to suit the changing conditions due to the introduction of the steam turbine and the gradual growth in the size of the units. The early types are now only found in museums and technical colleges, and new machines, whether built in this country, in America, in France or in Germany, are very similar in the general design, however they may differ in detail.

If at the present time it is decided to build a transmitting station for radio-telegraphy over several thousand miles, it is necessary to erect an aerial with a height say of 500 feet, and a capacity of 0.01 to 0.05 microfarad, and to supply this aerial with from 100 to 300 kilowatts at a frequency of 15,000 to 25,000 cycles per second with the provision of a suitable arrangement for signalling. There are several different methods in use at the present time for meeting these requirements, but it is obvious that they cannot all be of equal merit and it is a matter of some importance to determine as soon as possible which is the best method. If all the wireless telegraph companies in the world were to pool their experience and resources and be uninfluenced by considerations of patent rights and national prejudices, which system would be employed? Although the synchronous spark and the quenched spark appear to have been superseded for such large powers, the timed-spark system of the Marconi Company has recently been installed at the Norwegian transatlantic station at Stavanger. Arc generators have been carrying a large part of the transatlantic traffic between the United States and France and Italy and the new station at Bordeaux

is being fitted with a 1000 kilowatt arc supplied by the Federal Poulsen Company of America. An Alexanderson disc-inductor alternator generating directly the requisite frequency has been working at the New Brunswick station for some time, and no one can listen to the constant pitch of the note as received by the beat method without admiring the extremely accurate speed regulation. At Lyons the Société Française Radio-électrique have recently installed an inductor alternator of a different type, connected directly to the aerial and delivering thereto over 200 kilowatts. We understand that two 500 kilowatt machines of the same type are to be installed at Bordeaux. If this be so, arcs and high-frequency machines will be working side by side both at Lyons and Bordeaux. At Eilvese, near Hanover, the Goldschmidt internal cascade machine has worked throughout the war and is still in continuous operation. At Nauen the Telefunken Company has recently installed a new high-power plant consisting of an alternator giving 6000 cycles per second, connected to the aerial through two frequency doubling transformers in cascade, thus giving 24,000 cycles per second.

In addition to these half-dozen alternative systems all in actual operation, there is always the three-electrode valve, awaiting the successful design of a high-power type, but remaining for the present a matter of pious hopes and less pious rumours.

It will be seen that there is far greater diversity at the present day in the methods of generating high frequency currents than there ever was in the methods of generating low frequency currents, and there is little doubt that the future will see the elimination of some of these methods and the gradual improvement and standardisation of others.

It is probable that the power supplied to the aerial has now reached the highest value which will be required and that, with a higher efficiency of radiation of the transmitting aerial, and with greatly improved methods of eliminating atmospheric disturbances, and thus being enabled to use increased amplification, smaller transmitting powers will be found sufficient. For the present, however, the power required is several hundred kilowatts and the time seems ripe for a careful non-partisan comparison of the relative advantages and disadvantages of the various methods at present employed to produce this power.—THE EDITOR, *Radio Review*, July, 1920.

COMMERCIAL MANUFACTURE OF HELIUM.

A VERY interesting problem is presented by the possibility of the separation of helium from natural gases on a large scale. It is obvious that any process for accomplishing this separation must take advantage of the fact that helium remains a gas long after all the other constituents of natural gas have been liquefied. Two methods of concentrating the helium suggest themselves. First, the combustion method in which all inflammable constituents are removed by burning and the products of combustion are absorbed. This method involves the problem of disposing of the large quantity of heat liberated. This difficulty

might be met by burning the gas in an internal combustion engine, supplying at each explosion the oxygen necessary for the combustion of the gas. The energy thereby generated would be available for driving liquid air machines, dynamos for the production of oxygen by electrolysis, and other machinery required in the further processes. The products of combustion would be removed, the water by condensation and freezing and the carbon dioxide by chemical means or possibly also by freezing. The helium then remains mixed with small amounts of oxygen, hydrocarbons, and the original non-combustible gases. The further processes are suggested below.

The other method of concentrating the helium consists in applying a direct process of condensation. The gas is compressed and cooled as in the ordinary processes of liquefying air until all constituents whose boiling points are higher than that of helium are condensed. In order to do this economically it would probably be advisable to condense the gas by several stages—first to condense the hydrocarbons at as high a temperature as possible and then the nitrogen. Suitable temperature interchanges should be arranged so that the oncoming gas will be cooled on its way to the condenser by the evaporating condensate. The economy of the method depends largely on such an arrangement. In order to carry out the process advantageously the gas should be available at rock pressure, since thereby a large part of the cost of compression would be saved. The evaporating hydrocarbons could of course be returned to the mains so that waste of gas would be reduced to a minimum.

A rough estimate of the operating cost of separating helium in this manner may be made from the figures given by Claude on the cost of liquefying air ("Liquid Air, Oxygen, and Nitrogen," Churchill, London, p. 173). According to Claude the energy required to produce 1 litre of liquid air is 1.41 h.p.-hours and the cost is therefore about one penny.

About 600 litres of natural gas are required to produce 1 litre of liquefied gas, and the helium content of this quantity in the best sample examined is about 2 litres. Assuming that the cost of producing 1 litre of liquefied natural gas is the same as that of producing 1 litre of liquid air, then the helium can be manufactured at the cost of one halfpenny per litre or a shilling per cubic foot.

As a matter of fact it would likely be only a small fraction of this amount on account of the economy effected by the temperature interchangers mentioned above. This estimate is for the energy change alone, but that will probably be the important item in applying the process on a large scale.—*Bulletin No. 31, Department of Mines, Canada.*

THE INFLUENCE OF IONS ON THE OSMOTIC PRESSURE OF SOLUTIONS.

By JACQUES LOEB,

The Rockefeller Institute for Medical Research, New York.

I. THE osmotic pressure of solutions is usually measured indirectly, namely, by the determination of the freezing-point. Direct measurements have thus far been rare for the reason that it is difficult

to prepare membranes permeable for water but not for the solute. The measurements thus far obtained on non-electrolytes by Morse (1), and by the Earl of Berkeley (2) and their collaborators show that the actual values observed are not far from those expected according to van't Hoff's theory.

The difficulties in the preparation of semipermeable membranes are considerably diminished when we substitute colloidal solutions for solutions of crystalloids. By using solutions of proteins, collodion membranes satisfy the demand of semipermeability.

Gelatin is a very convenient protein for the purpose of such experiments. Like proteins in general, it is an amphoteric electrolyte being capable of forming salts with acids as well as with bases. The hydrogen ion concentration at which gelatin is neither in combination with acid nor with base is $10^{-4.7}N$ ($pH=4.7$ in Sörensen's logarithmic symbol). This hydrogen ion concentration is the isoelectric point. When acid is added to a solution of isoelectric gelatin, part of the acid combines with the gelatin to form gelatin-acid salts, and the proportion of isoelectric gelatin transformed into gelatin-acid salt increases with the amount of acid added. There exists always a definite equilibrium between free acid, gelatin-acid salt, and isoelectric gelatin. Since the physical properties of isoelectric gelatin are different from those of the gelatin-acid salt it is necessary to define a gelatin solution not only by the concentration of gelatin present but also by its hydrogen ion concentration. The writer was able to show that gelatin forms monogelatin salts with many dibasic or tribasic acids, e.g., oxalic, tartaric, and phosphoric acids, while it forms digelatin salts with sulphuric acid (3).

When we add a base, e.g., NaOH or Ca(OH)₂, to isoelectric gelatin, metal gelatinates are formed, and the relative amount of non-ionogenic gelatin transformed into metal gelatinates also depends upon the hydrogen ion concentration (4).

II. We can measure the osmotic pressure of gelatin solutions by putting them into collodion bags (cast in the form of Erlenmeyer flasks) closed with a rubber stopper perforated by a glass tube which serves as a manometer. A 1 per cent solution of gelatin to which a certain amount of acid or alkali had been added was put into the collodion bag which was dipped into a beaker containing water of the same hydrogen ion concentration as that inside the collodion bag. One per cent solutions of gelatin-acid salts had the highest osmotic pressure when the pH was about 3.4 and solutions of metal gelatinates had their highest osmotic pressure at a pH of about 8.4. At about 24° the permanent osmotic pressure was reached in less than 20 hours.

The influence of ions on the osmotic pressure of gelatin solutions was as follows:—

(1) The osmotic pressure of 1 per cent solutions of metal gelatinates of a pH of about 8.4 is a little over twice (but less than three times) as great when the metal is monovalent than when it is bivalent.

(2) The osmotic pressure of 1 per cent gelatin-acid solutions of pH 3.4 is a little over twice (but less than three times) as great when the acid anion is monovalent than in the case of SO₄.

(3) The addition of neutral salts or alkalis to

1 per cent metal gelatin solutions of ϕH 8.4 lowers the osmotic pressure of the solution and the depressing effect increases with the valency of the cation of the electrolyte added.

(4) The addition of neutral salts or acids to 1 per cent gelatin-acid solutions of ϕH 3.4 lowers the osmotic pressure of the solution and the depressing effect increases with the valency of the anion (5).

This influence of electrolytes on the osmotic pressure of gelatin solutions has no connection with the fact that gelatin is a colloid (6). This latter fact plays only a technical rôle in our experiments since it makes it easy to find a strictly semipermeable membrane. The writer has been able to show that the influence of ions on the osmotic pressure of gelatin solutions is connected with the existence of an electrical double layer at the boundary of watery phase and collodion membrane, whereby the water diffuses into the solution in the form of electrified particles.

III. When we separate a solution of a non-electrolyte like cane-sugar from distilled water by a collodion membrane, water diffuses into the solution with an initial velocity which is (up to gram molecular concentrations) a linear function of the concentration of the solute. When we separate a solution of an electrolyte from distilled water by a collodion membrane, water diffuses also into the solute but with an initial velocity which for lower concentrations of the solution is no longer a linear but a more complicated function of the concentration and the nature of the ions. The facts observed can be expressed in the following rules:—

(a) When pure water is separated from a solution of an electrolyte by a collodion membrane, water diffuses into the solution as if its particles were positively charged and as if they were attracted by the anions and repelled by the cations of the solution with a force increasing with the valency and another constitutional quantity of the ion.

(b) When the collodion membrane has previously been dipped for a short time into a solution of a protein and if the protein solution is then removed, Rule *a* holds also except that in the presence of hydrogen ions and of simple cations with a valency of 3 or above, in sufficient concentration, the particles of water diffuse into the solution as if they were negatively charged and as if they were attracted by the cation and repelled by the anion of the electrolyte with a force increasing with the valency and another property of the ion.

(c) The relative influence of the oppositely charged ions of an electrolyte is not the same for different concentrations of an electrolyte. At lower concentrations the influence of that ion prevails which has the opposite sign of charge as the watery phase, while in higher concentrations (of many, but possibly not of all electrolytes), the effect of the other ion prevails. The turning point lies for a number of electrolytes at a molecular concentration of about $M/256$. Finally a concentration is reached where this ionic influence on diffusion ceases and the gas pressure effect prevails (7).

These three rules apply also to solutions of gelatin salts. In the case of gelatin-acid salts

water is negatively charged and is attracted by the gelatin ion (which is positively charged) and repelled by the acid anion. This repulsion is greater when the anion is bivalent (SO_4) than when it is monovalent, *e.g.*, Cl . Hence the initial rate of diffusion of water into the gelatin-acid solution is greater in the case of gelatin chloride or gelatin nitrate, &c., than in the case of gelatin sulphate.

In the case of metal gelatinates the particles of water diffusing through the membrane are positively charged and attracted by the gelatin anion and repelled by the cation with which the gelatin is combined. This repelling effect is greater in the case of bivalent cations (Mg , Ca , Ba , &c.), than in the case of monovalent cations (*e.g.*, Li , Na , K , NH_4). Hence the initial rate of diffusion of water into solutions of metal gelatinates is greater in the case of sodium gelatinates than in the case of calcium gelatinates. When we add an electrolyte to the solution of a gelatin salt the increase in concentration of electrolyte brings about the depressing effect of that ion which has the same sign of charge as the electrified watery phase, as expressed in Rule *c*.

The permanent osmotic pressure of a solution separated from pure water by semipermeable membrane is that pressure which has to be applied to the solution side in order to cause equal numbers of particles of water to pass simultaneously through the membrane in opposite directions. It follows from this that the relative influence of electrolytes must be the same on the permanent osmotic pressure as on the initial velocity of diffusion through the membrane from pure water to solution, and this was found to be the case with the solutions of gelatin salts.

IV. The terms "attractive and repulsive effect" of the ion on the charged particles of water served the purpose of simplifying the presentation of the facts observed. In reality the "attractive and repulsive effect" of ions as expressed in Rules *a*, *b*, and *c* are the expression of an additive effect of the oppositely charged ions of an electrolyte on the density of charge of the double layer formed at the boundary of collodion membrane and watery phase. This was proved by experiments on electrical endosmose. When the collodion membrane is bounded on both sides by identical solutions, an equal number of particles of water will diffuse in opposite directions through the collodion membrane. When, however, an external potential difference is produced on the two sides of the membrane, an electrical endosmose will be established to one of the two electrodes according to the sign of the electrification of the watery phase in contact with the collodion membrane. By this method I ascertained the influence of electrolytes on the sign of charge on the watery phase which was expressed in Rules *a*, *b*, and *c*.

Cases of abnormal of osmosis, *e.g.*, the fact that liquid diffuses through parchment membranes from oxalic acid into pure water, had been known for more than 50 years, and it had been suggested by several authors, Girard, Bernstein, Bartell and Hocker, and Freundlich (8), that potential differences on both sides of the membrane caused these anomalies. To prove this view it was necessary to measure these potentials. Direct measurements of such potentials have been made by Girard, by Bartell and Hocker (8), by T. Ham-

burger (9), and by the present writer (as yet unpublished), but the results have thus far not been satisfactory. One can, however, test the idea indirectly by experiments on electrical endosmose. This method of verification seemed to be confronted with a serious difficulty. The influence of ions on electrical endosmose has been investigated by Perrin (10), who found that only one of the oppositely charged ions of an electrolyte, namely, the one which has the same sign of charge as the watery phase, has any influence (namely, a retarding one) on the velocity of endosmose, while the ion with the opposite charge has no influence. In my experiments on common osmose both ions of an electrolyte influenced the rate of diffusion of water simultaneously but in an opposite sense (as stated in Rules *a*, *b*, and *c*). I have investigated the influence of ions on the rate of electrical endosmose and found that Perrin's rule does not hold for collodion membranes, but that the Rules *a*, *b*, and *c* express not only the influence of ions on the transport of water through collodion membranes in common osmosis but also in the case of electrical endosmose.

According to the formula of Helmholtz as modified by Perrin, we know that in the case of electrical endosmose the following relation holds:

$$v = \frac{9 \cdot e \cdot E \cdot D}{4 \pi \cdot \eta \cdot l}$$

where v is the quantity of liquid carried electro-osmotically, e is the potential difference between the two strata of the double layer, E the external electromotive force, D the dielectric constant of the medium, η the coefficient of internal friction, and l the distance of the external electrodes.

In our experiments all quantities occurring in the formula except v and e were kept approximately constant. If the theory of Helmholtz is correct, we must, therefore, attribute the influence of ions on the rate of transport of water in electrical endosmose to their influence on e , *i.e.*, the density of charge on the watery phase; and since moreover, my experiments show that the influence of ions is the same for electrical and for free endosmose through collodion membranes, we must conclude that the influence of ions on the initial rate of diffusion and on the osmotic pressure of a solution is due to the influence of ions on the density of charge in the double layer at the boundary of watery phase and membrane.

V. This permits us to define more accurately the influence of ions on osmotic pressure. At the boundary of a membrane and liquid an electrical double layer is formed. In the case of collodion membranes the latter usually assumes a negative charge while the watery phase assumes a positive charge. When the collodion membrane is bounded on one side by pure water, on the other by a solution of an electrolyte, the anions of the latter increase the negative charge on the membrane and the cations diminish it, both effects increasing with the valency and another property of the ions. At lower concentrations of the electrolyte the influence of the anion increases more rapidly with increasing concentration of the electrolyte than the depressing effect of the cation, while at higher concentrations the reverse occurs. The turning point lies for a number of electrolytes at a molecular concentration of about $M/26$. Positively charged particles of water in the pores or inter-

stices of the membrane will be driven to that side of the membrane which is more negatively charged. Since this is usually the solution side, water will be driven from the side of pure water into the solution. When, however, the membrane has a higher negative charge on the side of pure water, the flow of the positively charged liquid through the membrane will be from the side of the solution to that of pure water (negative osmosis). This occurs in the case of solutions of $(CaOH)_2$ and $Ba(OH)_2$, when the concentration exceeds $M/256$.

When the collodion membrane has been treated with a protein, it is also generally negatively charged except when the solution contains hydrogen ions or simple trivalent or tetravalent cations beyond a certain concentration (which for H is $10^{-4} \cdot N$); in this case the membrane is positively and the watery phase is negatively charged. If we add in this case an electrolyte to the water the charge on the membrane is increased by the cations and diminished by the anion of the electrolyte, both influences increasing with the valency of the ion, and another property which is still to be defined. In lower concentrations the influence of the cation increases more rapidly than that of the anion, in higher concentrations of the electrolyte the reverse is true. Whenever the positive charge on the solution side of the membrane is greater than on the opposite side, the negatively charged particles of water will diffuse from the side of pure water to the side of solution. When, however, the positive charge on the solution side of the membrane is less than that of the side of pure water, the negatively charged layer of liquid will flow through the membrane from the side of the solution to that of pure water (negative osmosis). This will happen especially in the case of dibasic or tribasic acids when the concentration exceeds a critical limit. (Since the collodion membrane is permeable for electrolytes we are dealing in reality not with pure water separated by the membrane from solution, but with the condition of weak solution separated from a more concentrated solution).

It is obvious that with increasing concentrations of the solution the opposite effects of the oppositely charged ions of an electrolyte on the density of charge of the double layer tend to become equal and then the gas pressure becomes the main or only driving force for the diffusion of water into solution. For lower concentrations of electrolytes the algebraic sum of both forces, the differences of potential on both sides of the membrane and the gas pressure effect, determine the rate of diffusion of water through a membrane into a solution.

The new experiments on which these conclusions are based will appear in the *Journal of General Physiology*.

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- (2) Earl of Berkeley, and Hartley, E. G. J., *London, Proc. R. Soc. (A)*, 1916, xcii., 477.
- (3) Loeb, J., *J. Gen. Physiol.*, 1918-19, i., 559.
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- (5) Loeb, J., *Ibid.*, 1919-20, ii., 87, 273.

(6) The influence of electrolytes on the osmotic pressure of gelatin is not due to differences in the degree of electrolytic dissociation of the gelatin salts, since, *e.g.*, Na gelatin and Ca gelatin of the same concentration of gelatin and hydrogen ions have practically the same conductivity (4).

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RUSSIA'S CONTRIBUTION TO SCIENCE.*

By ALEXANDER PETRUNKEVITCH, Ph.D.

(Continued from p. 58.)

CHRISTOPHER Yakovlevitch Gobi, another student in algæ, born in 1847, made numerous contributions to our knowledge of the marine flora of the Gulf of Finland, of the White Sea, and other Russian seas. In more recent years a great deal of work has been done by various Russian botanists on local floras taxonomy and geographical distribution of plants, much of this work having been published in Russian journals.

Anatomy and physiology of plants have also found many distinguished investigators among Russian botanists. Andrei Sergeevitch Faminzyn, born in 1835, a student of Cienkowski's, is the first to be mentioned in this line. In his student years he published a "Natural History of the Conifers of the St. Petersburg Flora." But soon he turned his attention to physiological problems. In 1861 he printed an investigation entitled "An Attempt of a Chemico Physiological Investigation of the Process of Ripening in Grapes." He worked a great deal with algæ as material. In 1867 he published his paper "On the Action of Light on Algæ and other closely related Organisms." He extended these investigations to cover many forms, studying the formation of starch and other processes, dependent upon the action of light. In 1883 appeared his "Metabolism and Transformation of Energy in Plants." His paper on crystals and crystallites, published in German in 1884, was a natural sequence of these studies. In 1889 he published "A Contribution to the Question of Symbiosis between Algæ and Animals," followed in 1890 by an essay on "The Psychic Life of the Lowest Representatives of Living Beings." In 1898 he wrote an article "On Contemporary Natural Science and Psychology," and in 1901 on the "Reform of the System of Education in Russia."

Of his numerous students the best known are Batalin, Borodin, Baranetzky, Ivanovsky, and Timiryaseff. Alexander Fedoritch Batalin (born in 1847) published many investigations in cereals and other useful plants. But the work which attracted most attention was "On the Influence of Light on the Form in Plants" (1872) and "The Mechanics of Movement in Insectivorous Plants," mentioned by Charles Darwin in his books on the subject. Ivan Petrovitch Borodin (born in 1847) made investigations in the anatomy of plants, especially of their leaves, published in 1888 a well known "Course in Anatomy of Plants," studied the process of breathing, the formation and distribution of crystals in plants, &c.

Clementi Arcadiévitch Timiriaseff, born in 1843, is known by his studies of the chlorophyll. He discovered protophylline, a compound distinct from etioline and derived from the chlorophylline through reduction. Under the influence of light and air the oxidised protophylline becomes again chlorophylline. The absorption band of the protophylline being in the orange rays, Timiriaseff concluded that the orange rays are mostly responsible for the green colour in plants, a conclusion which later found confirmation in the experiments of the German scientist Reincke. But Timiriaseff's fame rests chiefly on his ability as a teacher, lecturer, and populariser. His book "The Life of the Plant" was published in several editions and has been translated into German. For many years he was professor of plant anatomy and physiology at the University of Moscow, beloved and admired by his students. A staunch supporter of Darwin he published a book in 1863 on "Darwin and His Theory" which has since seen many editions. He was violently opposed to Weismann's theories of heredity and I remember him attacking Weismann in his lectures with all the vigour of his eloquence. His works found him recognition on the part of the Royal Society which elected him Fellow.

Wladimir Paladin, born in 1859, is another of the well known contemporary Russian botanists of the older generation. He worked in anatomy and physiological chemistry of plants. His books "Plant Anatomy" and "Plant Physiology" are used as textbooks in all Russian universities and have seen several editions. Many of his investigations have for their subject metabolism in plants.

Of other Russian botanists whose work is known outside of Russia I may mention Belajeff, Nawaschin, Gorojankin, and Golenkin, as well as the distinguished bacteriologist Vinogradsky.

Zoology, embryology, and allied sciences have been always popular with the Russians. We have seen already that as early as 1725 Duvernoie was called to the first chair of anatomy and zoology established at the St. Petersburg Academy. Three names of men who, because of their Teutonic origin and great achievements in science are claimed by the Germans, may be even with greater justice claimed by Russia because they spent most of their life in Russia and became identified with the Imperial Academy of Petrograd. These are Wolff, Pallas, and Baer.

Kaspar Friedrich Wolff, who by right should be called the founder of the science of embryology, was born in Berlin in 1733, the son of a tailor. In Halle where he studied medicine he wrote his "Theoria generationis" published in 1759,

* From the *Transactions of the Connecticut Academy of Arts and Sciences*, June, 1920.

a remarkable work in which he attacked the so-called evolution or preformation theory and advanced his own theory of epigenesis or gradual development. Unable to continue his studies in Germany, Wolff gladly accepted a call to the St. Petersburg Academy in 1766. In 1768 and 1769 he published his second great work "*De Formatione Intestinalium*" in the *Memoirs of the Academy*. Von Baer spoke of this work as "the greatest masterpiece of scientific observation which we possess." Wolff died in St. Petersburg in 1794, and those Germans who claim him because of his origin and still more because of the excellence of his work, should remember the statement made by Ernst Haeckel himself in his *Natuerliche Schöpfungsgeschichte* that "*De Formatione Intestinalium*" remained unknown to the Germans until it was translated from the Latin in which it is written into German in 1812—which means that Wolff during his life did not exist for the Germans since he left Germany at the age of 33.

Peter Simon Pallas, born in Berlin in 1741, is also claimed by the Germans. Yet he left Germany when 20 years of age, lived in England where he was elected member of the Royal Society, then in Holland, served for a short time as professor of surgery in Berlin, and was called to the Imperial Academy of St. Petersburg in 1767, *i.e.*, at the age of 26 years. In Russia he spent 43 years, *i.e.*, until 1810, and when his wife died, returned to Germany only to die the following year. He was a great traveller and a prolific writer. Before going to Russia he published "*Elenchus Zoophytorum*" and "*Miscellanea Zoologica*." He began publishing his celebrated "*Specilegia Zoologica*" in 1767. The natural history results of his six years of travel through Russia and Siberia were published in the French translation of his "*Travels, &c.*" (eight volumes with nine volumes of plates, 1788-1793). He published "*Icones Insectorum præsertim Rossæ Siberique peculiarium*" in 1781-1806, and "*Zoographia russo-asiatica*" in three volumes, in 1811. His was a remarkable mind interested in many problems, he was an accomplished geologist and paleontologist, he studied the geographical distribution of animals, wrote a memoir on variation in animals, as botanist published the first "*Flora Rossica*" in two volumes in 1784-1788. He was besides a philologist, topographer, mineralogist, ethnographer, archeologist, agronomer, and technologist. He was well known in other countries, but although he did not particularly enjoy life in Russia, he spent most of it there, partly in travels, partly in research in his estate in the Crimea, which Catherine the Second presented to him.

Carl Ernst, or Carl Maximovitch von Baer, the father of embryology, was born a Russian subject in 1792 in Estland, Russia, and studied first at Reval at a gymnasium and then from 1810 to 1814 at the University of Dorpat. His work is too well known to need any particular mention here. What I want however to point out is that Baer, like Wolff and Pallas, spent most of his life in Russia. In Germany he spent only seventeen years as professor at Königsberg, from 1817-34, when he was called for the second time to the St. Petersburg Academy. (He was called the first time in 1829, but returned from St. Petersburg to Königsberg in 1830). From now on to the end of his life, *i.e.*, forty-two years, he lived

in Russia and worked there, dying in Dorpat in 1876. Thus even the second volume of his celebrated "*Embryology of Animals*," published in 1837, appeared three years after his departure from Germany. And his discovery of the mammalian egg in 1827 was also for the first time reported in a communication to the St. Petersburg Academy. Baer was a many-sided investigator, traveller, anthropologist, ethnographer, historian, and geographer. Some of his investigations were written in the Russian language, including the especially important paper "Why have our rivers which flow north or south, a high right and low left shore," in which he established the law of meridional deviation of rivers usually known as Baer's Law.

Johann Friedrich, or better Fedor Fedorovitch Brandt, born in Germany in 1802, was called to Russia in 1831 and became director of the Zoological Museum of the St. Petersburg Academy. During the forty-eight years of his life in Russia he wrote a number of papers in Latin and German on the subject of systematics, anatomy, paleontology, and geographical distribution. His son Alexander Fedorovitch Brandt, born in St. Petersburg in 1844, and for years professor of zoology at the University of Kharkov, is known for his work on the Anatomy of Invertebrates and especially on the structure of the reproductive system in insects as well as the development of round worms.

The problems of anatomy have occupied and are still occupying the attention of many investigators. Such men as Kowalewsky, Metchnikov, Salensky, Bobretzky, Korotneff, Tikhomirov, Zograf, Kulagin, Schimkevitch, Cholodkowsky, Schewiakow, W. Wagner, Kojevnikov and others have published papers on the one or the other invertebrate group, and Menzbir, Koltzoff, Ivantzoff, Nassonow, Sushkin on the anatomy of vertebrates. The subject, however, does not lend itself easily to a general account and I shall merely remind the reader of the interesting descriptions of the two creatures forming a transitional stage between the comb-jellyfish and the flat worms. One of these papers was written in Russian by A. Kowalewsky and is entitled "*Cæloplana Metschnikowii*," and has been published in the *Proceedings of the Society of Friends of Natural Science in Moscow*, in 1882 (a preliminary account was published by Kowalewsky in German in 1880). The other belongs to A. Korotneff, is entitled "*Ctenoplana Kowalewskii*," and was published in German, in the *Z. f. W. Z.* in 1886. Of great interest is also the work of Knipowitsch on the strange group of Ascithoracida among the Cirripedia.

Microscopic anatomy and histology have also been made subjects of extensive studies. The microscopic structure of invertebrates is generally treated by zoologists, but what is known as the department of histology in Russia has to deal almost exclusively with vertebrates. Here the names of Owsjannikov and Lawdovsky are first to claim our attention, especially because of their remarkable textbook "*Microscopic Anatomy of Man and Animals*," published in two large volumes in 1887-8 in co-operation with Dogiel, Erlitzky, Peremeschko, and Stieda, all of whom were at that time professors in various Russian universities (Stieda was professor at Dorpat). I

also wish to mention the excellent textbook in cytology written by Ogneff, and published in 1903.

The study of systematics, zoogeography, and local faunas was continued uninterruptedly since the first works of Pallas. The museums in Petrograd, Moscow, and other universities were enriched by numerous collections (of special interest is the *Equus Przewalskii*). Articles treating special groups of animals are found in all Russian periodicals. The study of fishes was always popular in Russia. We find the excellent monograph on the "Bieluga" written by Sabaneeff in 1871 and his "Fishes of Russia" published in 1875. In more recent years my classmate Berg has distinguished himself as a student of Russian and Asiatic fishes. Of the books on Russian birds I should like to mention only the classical two volumes by Menzbir which embody all our knowledge of the life and system of that group, and the books of Modest Bogdanoff.

The impetus given by Baer through his discovery of the germ layers, directed the attention of zoologists toward the problems of embryology. Here the names of Metchnikoff and Kowalewsky occupy quite an enviable position. Alexander Onufrievitch Kowalewsky was born in 1840 and at first studied engineering. His first work in embryology, published in 1865, on the "History of Development of *Amphioxus lanceolatus*" at once placed him in the ranks of distinguished investigators. Equally fine was his thesis for the degree of Doctor of Zoology, "On the Development of *Phoronis*," published in 1867. In the next year Kowalewsky was called to the chair of zoology at Kazan, a year later to Kiev. The year after he undertook a scientific journey to the Red Sea and Algiers. Returning, he was appointed professor at the University of Novorossiisk and in 1890 member of the St. Petersburg Academy and in 1891 professor of histology at the University of St. Petersburg. His investigations cover almost the entire field of invertebrate embryology and in view of their importance it would be almost impossible to point out any title in preference to others. We may, however, mention his "Embryology of Simple Ascidians," published in 1866, an epoch-forming work because in it the Ascidians were for the first time shown to be of chordate nature; his "Embryological Studies on Worms and Arthropods" published in 1871, a work which received the prize of the St. Petersburg Academy and which contained besides other interesting observations, the celebrated description of the development of *Sagitta*; and some of his later publications on the physiology of excretory and circulatory organs in invertebrates.

Ilya Ilyitch Metchnikoff was born in 1845 and studied at Kharkov. From 1864 to 1867 he worked in Germany at various universities. His first important publications published in 1866 deal with the development of insects. His work in zoology extends over about twenty years before he changed from zoology to bacteriology and immunity. His influence on the development of our knowledge of invertebrate embryology was no less than that of Kowalewsky and his researches also cover almost all groups of invertebrates. He was the first to give a careful description of the development of Hydrozoa and proposed the term of Parenchymula for their early larvæ. He described parthenogenesis or as he terms it "Sporo-

gony" in *Cunocanta*. He gave the first remarkable description of the embryology of the scorpion. He described the six-legged larva of the Diplopoda. In his "Embryological Studies of Insects," published in 1866, he described the early separation of the progenital cells which he termed the "poiecels" in parthenogenetic Diptera. It was while working on the development of invertebrates that Metchnikoff discovered phagocytosis in 1882, the discovery which proved of such vital importance in the study of disease and immunity and which gradually diverted his attention from purely zoological subjects. But Metchnikoff worked also in anthropology and published in 1874 and in 1876 investigations of the Kalmyks. He was also a populariser of biology and wrote numerous articles published in the Russian magazines: "Naturalist," "Vestnik Evropy," "Nature," "Home and School."

The brilliant young zoologist Alexander Pavlovitch Fedchenko, who perished at the age of 29 in a snowstorm on Mont Blanc in 1873, has left a few remarkable investigations, as for example, the description of the life history, hitherto unknown, of the Guinea worm, *Dracunculus medinensis*. He brought from Turkestan a rich collection of animals and plants, the description of which was published later in Russian journals. The wife of Fedchenko continued his studies in plants and published numerous papers of a taxonomic and phytogeographic character.

I have already mentioned the discovery of paedogenesis by Nicolai Petrovitch Wagner in 1861, such a startling discovery at the time that von Siebold refused to print the paper until the German zoologist Pagenstecher two years later made a similar observation. But Wagner's paper was meanwhile printed in Russian and received a prize.

The discovery of artificial parthenogenesis was also made for the first time by a Russian, my teacher Alexander Andreevitch Tikhomirov, in 1881, on the eggs of *Bombyx mori*, the silkworm. To him belongs also the best monograph on this insect, unfortunately unknown to foreigners because written in Russian, in 1882, and he was the first to introduce *Scorcionera* as food-plant for silkworms instead of the mulberry which cannot grow in the far north. By this substitution of food Tikhomirov made sericulture possible in North Russia and Finland. In 1887 he published also in Russian, an interesting investigation in the development of Hydrozoa. A man of extraordinary education and wide knowledge, Tikhomirov was unfortunately misled by ambition, diverted his activities into administrative channels and cast a shadow on his name as investigator through his co-operation with the secret service while Acting President of the University of Moscow. But the little that he published will endure and is to the credit of Russian science.

Salensky, Korotneff, Cholodkovsky, and Schimkevitch as well as others have contributed to our knowledge of the development of various animals. The anatomy and development of spiders, for example, was for a long time almost entirely based on the studies of Schimkevitch and his "Text-book of Comparative Anatomy" has been translated into German. Cholodkovsky was the first to elucidate the complicated life history of Scale-Insects in a series of articles.

A host of younger scientists were engaged in research in their respective sciences when the world war claimed the attention of all patriotic men. As I have explained before, in Russia, men espousing an academic career were exempt from service and therefore did not, in the majority of cases, receive any military training whatsoever. But many men of science volunteered their services in other capacities than soldiers. The revolution of 1917 brought new hopes, but these were soon shattered, and now the universities are deserted and empty but for a few who have adapted themselves to the Bolshevik régime or chose to remain at their posts and to carry on the torch of light amidst the darkness of ruin and desolation. Some perished. Others fled to foreign countries. Russia's contribution to science may become a closed chapter, unless new forces will arise capable not only of adjusting themselves to the new conditions, but of creating and producing where the present generation has failed.

RESULTS ACHIEVED IN INDUSTRY BY MODERN METHODS.*

By J. F. BUTTERWORTH.

SINCE I am here to-night as the result of your invitation sent through the Industrial League and Council, to address you upon "Modern Methods in Industry," a few words of explanation as to the aims of this body may not be out of place. Its Presidents are: The Right Hon. J. H. Whitley, M.P., Deputy Speaker, and the Right Hon. G. H. Roberts, M.P., former Food Controller.

The chief aim of the Industrial League and Council is to bring the employer and employed together in an atmosphere conducive to a calm and fruitful discussion of industrial problems in which they are mutually interested. The League also assists in establishing Whitley Councils and Works Committees, believing that by such methods the interests of industry can best be served. Its functions are purely educational and not executive.

The League does not interfere between the Employers' and Labour Organisations, nor take any part in trade disputes. It is, however, ready at all times to place any information in its possession at the disposal of the Employers' Associations and Trade Unions. Members, therefore, are able to discuss industrial questions of mutual interest with greater freedom and sincerity than would be possible if they felt that they were committing their respective organisations. The main thing we have to bear in mind is that to save our country we must all pull together. We had all classes fighting and dying together during the war. Why not therefore have the same united effort for peaceful industry?

The Industrial League and Council is composed of employers and employed, who know the great advantage it is to Industry to have complete accord and co-operation within its ranks. Its great activity has been followed by the success it deserves, and every citizen who has at heart the peaceful and prosperous development of his country should not hesitate to join its ranks and do something towards the attainment of its great object.

Dr. Russell Wakefield, Bishop of Birmingham, has said:—"It is the sanity of the Industrial League and Council which appeals to me so strongly. To-day the nation is abnormal, the tendency of everybody is towards something ill-considered and rash, and I do see in the Industrial League and Council work, above all, sanity."

Fifty-four Whitley Councils have been already inaugurated by as many different industries, and although the men who make the barrels for your beer have joined in the scheme, the brewers and maltsters are as yet absent from the list.

It will be impossible to sustain the financial burdens imposed by the war unless our rate of wealth production is greatly increased. This can be accomplished only by giving the worker a larger interest in the business in which he is engaged, and by raising the scale and efficiency of our industrial activities to an extent not contemplated in pre-war days. In order to bring about this extension and increased efficiency, many changes and re-adjustments will have to be made in the industrial world.

I am obliged for the opportunity given me to-night to come and have a talk with you about "Modern Methods in Industry." All the results accomplished to date have come about through the study of the principles of scientific management described by the late Dr. W. F. Taylor, of Philadelphia, and their application to the industries by him and other able men, principally engineers.

The subject is so large and interesting a one that much time might be profitably spent in discussing its varied teachings, but to-night I merely touch upon some of its leading features. Even these, I trust, will be sufficient to give you serious food for thought, and create a desire for more knowledge of the whole movement and the economic revolution it is bringing about wherever its principles have been adopted and efficiently and thoroughly installed. Much has been written and illustrated about this subject, and those who may wish to know more of it can now get many good books, a perusal of which cannot but be beneficial and may be productive of far-reaching results. I shall be happy to furnish the titles and authors of the leading books to any person requiring them. There is confusion in many minds to-day as to the meaning of Scientific Management, but when I state that it is management based upon actual and accurate measurement, its scope and object will be made clear to such an audience as I am now addressing.

Its skilful application is an art that must be acquired, but its fundamental principles have the exactness of scientific laws, the study of which is open to all. There is nothing secret or hidden about it, for it is a science that is the result of accurately recorded, exact investigations, the results of which have been formulated and further findings are being added to it every day. The scope of this science is unlimited, for it applies to every field of activity, both mental and physical, and its laws are universal. Its fundamental aim is the elimination of waste of every kind with the attainment of the desired results by the least necessary amount of time and of effort; it may and often does result in expansion, but its primary aim is conservation and saving, by making adequate use of every particle of any type of energy expended.

* A Paper read before the Midland Counties Section of the Institute of Brewing, March 18th, 1920.

The old saying, "The proper study of mankind is man," has assumed new meanings since the votaries of this new science have divulged their findings to the world, for they have taught us that success in handling both the human and material elements depends upon exact knowledge of the element itself and the acquired experience as to how either or both can best be handled. Through motion, fatigue and time study the capabilities of the workers have been determined. The exactions of the work and the fatigue of the workers which result, together with the amount and nature of the rest to overcome such fatigue are known, and their practical application of the findings to the industries have been fraught with the happiest results to employers and employed alike, for they have increased output, decreased working costs, and added to the wages earned by the workers. Agriculturists have taught us that it is possible to get great annual outputs and conserve producing force unimpaired by judicious use of suitable fertilisers. The knowledge of how to keep the soil at its fullest producing capacity, making provision for depleted energy, is largely standardised and widely practised. Industrialists should realise these facts and apply them to their workers. The sooner these workers can be treated to overcome fatigue and regain their normal working capacity in the shortest possible time, the quicker will the toiling masses and their employers benefit. Suitable provision for such recovery in the industries, before the days of scientific management, was unknown.

I therefore appeal to all to increase their knowledge of industrial conditions and necessities so as to increase production, which alone can prevent disaster and ruin to the nation.

Friends of the workers can do good service by teaching the truth as to the benefits obtainable from increased outputs, for these latter are the one condition that will permit a permanent rise in wages and at the same time reduce production costs. The benefits to the worker of increased wages speaks for itself, but the benefits to him of reduced cost of production are less obvious. However, they are just as real, for when production costs are lowered, it means greater purchasing power of the workers' wages; in other words, the first aim of the increased production campaign—reduced cost of living.

By what means is the cost of living going to be reduced? Some people will tell you that it cannot be reduced because every time wages are increased to meet the higher cost of living, prices are put up to overtake the increased cost of labour. But the cost of living can be reduced if the costs of production are kept in check by the installation of scientific management, with its later additions, throughout all industries.

The management of all works, great or small, must realise it is absolutely necessary that a "thinking and planning" department be established in the very beginning. If any person's ambition leads him to win races or other athletic contests, he can find out the recorded times of performances of previous champions; and if he desires to lower the record, he knows exactly the time he has to beat, and practises and trains accordingly. The annals of sport are full of such records. Can any of you tell me where such records are available

to the industrial worker anxious to improve his craft skill, and earn more money? Which of such records would be most productive of material prosperity and happiness to the nation? The records were not taken in the case of the athlete to "speed-up" or "drive" him, but to co-operate with him in showing what was reasonably attainable.

(To be continued).

CORRESPONDENCE.

CLAYS AND ELECTRICAL OSMOSIS.

To the Editor of the Chemical News.

SIR,—The paper on the above subject in this Journal of July 9, 1920, p.14, by Messrs Highfield, Ormandy, and Northall-Laurie, raises some interesting questions, possibly of considerable commercial importance.

It is well known that the Austrians have been able to obtain shapes commercially by special moulding which manufacturers in this country will not undertake.

It may be that the clay itself has something to do with the success of the process. I understand that the clay is forced into specially constructed moulds.

It would be interesting if someone familiar with the Austrian methods could throw some light on this phase of the subject.

The colour of china is also of possible interest, but I believe this is due to the place of origin of the clay materials, as the English product is free from the bluish-white cast common to the Austrian product; a difference connoisseurs notice at once, preferring the English whiteness. At any rate, this is a point of interest in connection with the process quite apart from any metallic colourings.

Technical literature is often disappointing, as trade secrets, if published at all, are often so distorted as to be of little value. If these points could be elucidated, even if they are not new to the expert, they would be appreciated, I believe, by the general reader who is anxious to extend his knowledge in such directions.—I am, &c.

F. H. LORING.

NOTES.

INSTITUTE OF CHEMISTRY.—(*Pass List. July (1920) Examinations*).—The results of the examinations of the Institute recently held in London, Manchester, and Glasgow have now been published. The following candidates were successful:—For the Fellowship: In the Branch of Metallurgical Chemistry—A. C. Melville; in the Branch of the Chemical Technology of Textiles—G. E. Knowles. For the Associateship: In the Branch of Mineral Chemistry—E. A. Morris; in the Branch of Metallurgical Chemistry—C. Hollingsworth; in the Branch of Organic Chemistry—

L. V. Cocks and R. G. M. Dakers; in the Branch of the Chemistry of Food and Drugs, &c.—S. Greenberg, Vera Newcombe, and H. C. M. Winch; in the Branch of the Chemical Technology of Coal Tar Dyestuffs—A. Potter. The following Associates have passed the Examination for the Fellowship and will be entitled to apply for election to the Fellowship on the completion of three years' registration as Associates: In the Branch of Agricultural Chemistry—G. G. Auchinleck and H. C. S. de Whalley.

EMPIRE MOTOR FUELS.—The Empire Motor Fuels Committee of the Imperial Motor Transport Council has recently co-opted Mr. Sam Henshaw, F.I.C. (National Benzole Association) and Professor H. B. Dixon, F.R.S. (Manchester University) as additional members, and has appointed the following Sub-committees:—Engineering: Dr. W. R. Ormandy, D.Sc., F.I.C. (Chairman), Col. D. J. Smith, O.B.E., M.I.A.E., Mr. G. W. Watson, M.I.Mech.E., M.I.A.E., Mr. G. J. Shave, M.I.Mech.E., M.I.A.E., Mr. F. G. Bristow, F.C.I.S., F.S.S., A.M.Inst.T. (Hon. Secretary). Denaturation:—Sir Charles Bedford, LL.D., D.Sc. (Chairman), Dr. W. R. Ormandy, D.Sc., F.I.C., Mr. Sam Henshaw, F.I.C., Mr. F. G. Bristow, F.C.I.S., F.S.S., A.M.Inst.T. (Hon. Secretary). Sir James Dobbie, F.R.S., the Government Chemist, has given the Committee permission to reprint and circulate his report, furnished to Mr. Walter Long's Committee last year, on Denaturants and Denaturing, and as from the first prox. the Committee will undertake its own research in these important branches of investigation.

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OWING to the greatly increased cost of printing and paper, and the advance in the postal rates, we have been compelled to raise the price of the **CHEMICAL NEWS** from 4d. to 6d. (by post 7d.). The new subscription rates are as follows:—

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3148.

REPORT OF THE INTERNATIONAL
COMMITTEE ON ATOMIC WEIGHTS FOR

1920-1921.

SINCE the report of this committee for the preceding year was prepared, only a few new determinations of atomic weights have been published. They may be summarised as follows:

Fluorine.—Moles and Batuecas (*J. Chim. Phys.*, 1919, xvii., 538) have made twenty-three determinations of the density of methyl fluoride, CH_3F . For the weight of a normal litre of the gas, they find, in mean, 1.54542 grms. From this the molecular weight, 34.024, is deduced, and $\text{F}=18.996$. This, rounded off to 19, is the value already accepted.

Silicon.—Baxter, Weatherill, and Holmes (*J. Amer. Chem. Soc.*, 1920, xlii., 1194), from analyses of silicon tetrachloride, find $\text{Si}=28.111$. This determination, however, is not regarded by the authors as final. Its acceptance, therefore, must await confirmation, especially as the value is much lower than that given in the present table of atomic weights.

Lead.—The atomic weight of isotopic lead from thorium minerals has been determined by Hönigschmid (*Zeitsch. Elektrochem.*, 1919, xxv., 91). For lead from Norwegian thorite, he finds $\text{Pb}=207.88$ to 207.92 . For lead from Ceylonese thorianite, $\text{Pb}=206.88$ to 207.24 . In thorianite, there is evidently a mixture of isotopes, and perhaps also of normal lead.

Richards and Sameshina (*J. Amer. Chem. Soc.*, 1920, xlii., 929) have examined lead from a radioactive Japanese mineral. The values found for the atomic weight were 207.11, 207.12, and 207.15. For ordinary lead, the corresponding value was 207.184. The Japanese material, evidently, contained very little isotopic lead.

Tin.—In two papers, Brauner and Krepelka (*ibid.*, dccccvii., 928) give new determinations of the atomic weight of tin based upon analyses of the tetrabromide. In the first paper, which is preliminary, they find $\text{Sn}=118.70$. In the second, by Krepelka alone, the value $\text{Sn}=118.699$. This confirms the earlier determinations by Briscoe and by Baxter and Starkweather. The work of the last-named chemists appears in full in the same number of the *Journal*. It was noticed in our last report from a preliminary publication.

Tellurium.—From analyses of the hydride, TeH_2 , Bruylants and Michielsen (*Bull. Acad. roy. Belg.*, 1919, Nos. 2-3, 119) find for tellurium the values $\text{Te}=127.73$, 127.79 , and 127.4 . The last value they reject. As these determinations are preliminary, they need no further consideration now.

Scandium.—Meyer and Schweig (*Zeitsch. anorg. Chem.*, 1919, cviii., 303), after a study of methods for the purification of their material, give determinations of the atomic weight of scandium by the usual sulphate method. They found $\text{Sc}=45.03-45.37$, in mean 45.23 , but conclude that the method is untrustworthy. Hönigschmid

(*Zeitsch. Elektrochem.*, 1919, xxv., 93), with some of the same material, prepared scandium bromide and determined its ratio to silver. In eighteen concordant analyses, he found $\text{Sc}=45.099$, which may be rounded off to 45.1 . This value is accepted by Meyer and Schweig, and should be adopted.

Samarium.—The atomic weight of samarium has been determined by Owens, Balke, and Kremers (*J. Amer. Chem. Soc.*, 1920, xlii., 515) by analyses of the anhydrous chloride. From the mean of eighteen concordant analyses, $\text{Sa}=150.43$, in close agreement with the determinations by Stewart and James, 150.44 , which was noticed in our report of last year.

Apart from the actual determination of atomic weights, three papers relative to the reduction of the experimental data deserve attention. Guye (*J. Chim. Phys.*, 1919, xvii., 171), in one paper, has discussed the application of Avogadro's law to this problem. In a second paper (*ibid.*, 141), he has examined the data relative to bromine and silver, and concludes that $\text{Br}=79.92$ and $\text{Ag}=107.87$. The last figure differs from the value 107.88 , as given in the table, by only 0.01 , which is quite within the limits of experimental uncertainty. The third paper, by Van Laar (*ibid.*, 266), relates to the method of calculating atomic weights.

The only change in the table of atomic weights is in the case of scandium—from 44.1 to 45.1 —which appears to be fully justified by the evidence.

(Signed) F. W. CLARKE.

T. E. THORPE.

G. URBAIN.

1921. International Atomic Weights.

	Symbol.	Atomic weight.
Aluminium	Al	27.1
Antimony	Sb	120.2
Argon	A	39.9
Arsenic	As	74.96
Barium	Ba	137.37
Bismuth	Bi	208.0
Boron	B	10.9
Bromine	Br	79.92
Cadmium	Cd	112.40
Cæsium	Cs	132.81
Calcium	Ca	40.07
Carbon	C	12.005
Cerium	Ce	140.25
Chlorine	Cl	35.46
Chromium	Cr	52.0
Cobalt	Co	58.97
Columbium	Cb	93.1
Copper	Cu	63.57
Dysprosium	Dy	162.5
Erbium	Er	167.7
Europium	Eu	152.0
Fluorine	F	19.0
Gadolinium	Gd	157.3
Gallium	Ga	70.1
Germanium	Ge	72.5
Glucinum	Gl	9.1
Gold	Au	197.2
Helium	He	4.0
Holmium	Ho	163.5
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.92

	Symbol	Atomic weight.
Iridium	Ir	193.1
Iron	Fe	55.84
Krypton	Kr	82.92
Lanthanum	La	139.0
Lead	Pb	207.20
Lithium	Li	6.94
Lutecium	Lu	175.0
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.6
Molybdenum	Mo	96.0
Neodymium	Nd	144.3
Neon	Ne	20.2
Nickel	Ni	58.68
Nitron (radium emanation)	Nt	222.4
Nitrogen	N	14.008
Osmium	Os	190.9
Oxygen	O	16.00
Palladium	Pd	106.7
Phosphorus	P	31.04
Platinum	Pt	195.2
Potassium	K	39.10
Praseodymium	Pr	140.9
Radium	Ra	226.0
Rhodium	Rh	102.9
Rubidium	Rb	85.45
Ruthenium	Ru	101.7
Samarium	Sa	150.4
Scandium	Sc	45.1
Selenium	Se	79.2
Silicon	Si	28.3
Silver	Ag	107.88
Sodium	Na	23.00
Strontium	Sr	87.63
Sulphur	S	32.06
Tantalum	Ta	181.5
Tellurium	Te	127.5
Terbium	Tb	159.2
Thallium	Tl	204.0
Thorium	Th	232.15
Thulium	Tm	168.5
Tin	Sn	118.7
Titanium	Ti	48.1
Tungsten	W	184.0
Uranium	U	238.2
Vanadium	V	51.0
Xenon	Xe	130.2
Ytterbium (Neoytterbium)	Yb	173.5
Yttrium	Yt	89.33
Zinc	Zn	65.37
Zirconium	Zr	90.6

HYDRATION AS AN EXPLANATION OF THE NEUTRAL SALT EFFECT.

By JOHN ARTHUR WILSON.

A MASS of experimental data now available seems to indicate that the addition of sodium chloride to an acid solution results in an increase in hydrogen-ion concentration, whereas adding it to an alkaline solution causes an increase in concentration of the hydroxide ion. (Poma, *Z. physik. Chem.*, 1914, lxxxviii., 671; Arrhenius, *ibid.*, 1899, xxxi., 197; Harned, *J. Am. Chem. Soc.*, 1915, xxxvii., 2460; Fales and Nelson, *ibid.*, 1915, xxxvii., 2769; Thomas and Baldwin, *ibid.*, 1919, xli., 1981). This is of very great importance in the manufacture of leather, although probably not more so than in other fields of chemistry.

An interesting practical example of this property of salt is furnished by a series of experiments in chrome tanning recently carried out by the writer. A commercial chrome liquor (a solution of basic chromic sulphate and sodium sulphate) diluted to contain 17 grms. of chromic oxide per litre was found to be capable of completely tanning certain pickled calf-skins in less than 2 days without any addition of alkali. (The pickling process consists of subjecting unhaird skins to a bath of sulphuric acid and sodium chloride of definite strength until equilibrium is established. A piece of chrome leather is considered fully tanned when it will remain apparently unaltered in boiling water for 5 minutes. In tanning successive lots of skins with this liquor, no difficulty was experienced in maintaining conditions so nearly constant that no difference could be detected either in the rate of tanning or in the properties of the resulting leather. The experiment was then repeated with all conditions exactly the same as before except for the addition of one lb. of sodium chloride per gallon (120 grms. per litre) of chrome liquor. Measurements with the hydrogen electrode showed that an increase of about 50 per cent in hydrogen ion concentration resulted from this addition of salt. After the skins had been in the liquor for 7 days, they were still not tanned and it was necessary to add a considerable amount of alkali to bring about complete tannage. A very similar effect is produced by adding hydrochloric acid instead of salt.

The effect of sodium chloride upon alkaline solutions is shown by adding salt to a lime liquor, which consists of a solution kept saturated with calcium hydroxide by means of a large excess and containing a comparatively small amount of sodium sulphide. The function of this liquor is to destroy the Malpighian layer of the epidermis of the skins so that the hair may simply be rubbed off by working on a suitable machine. Adding salt to such a liquor was found to increase the plumpness of the skins and to cause the hair to slip somewhat more easily. This same effect is produced by the addition of sodium hydroxide.

The chrome tanning experiments noted above were a continuation of a series of simpler experiments by Wilson and Kern (*J. Am. Leather Chem. Assoc.*, 1917, xii., 445), of which the following is typical. 0.1/N sodium hydroxide was added to 10 cc. of a filtered chrome liquor, with suitable agitation, until the first permanent turbidity appeared, due to precipitation of basic chromic salts, the amount required being 3.7 cc. To another portion of 10 cc. was added 0.04 gm. molecule of sodium chloride; in this case 6.8 cc. of the standard alkali was required to start precipitation. Repeating the experiment, using in each case 10 cc. of the chrome liquor and 0.02 gm. molecule of added salt, Wilson and Kern found different salts to have very different degrees of effectiveness in preventing precipitation, the order being $KCl < NH_4Cl < NaCl < MgCl_2 < MgSO_4 < Na_2SO_4 < (NH_4)_2SO_4$. The liquor containing potassium chloride required only 4.0 cc. of 0.1/N sodium hydroxide to start precipitation against 11.6 cc. for ammonium sulphate.

The order of these salts led Wilson and Kern to the conclusion that the effect was probably due to hydration of the added salt. Chrome liquors

are all decidedly acid in reaction, and, if the added salt becomes hydrated at the expense of the solvent, the ratio of moles of acid to moles of solvent, and consequently the activity of the acid, will be increased, the more so the greater the degree of hydration of the added salt.

This explanation was regarded as sufficient until Thomas and Baldwin (*Loc. cit.*) proved by electrometric measurements that while chlorides actually do increase the hydrogen-ion concentration, not only of chrome liquors but of pure acid solutions as well, sulphates behave very differently, generally lowering the hydrogen-ion concentration, just the reverse of what might have been expected from the results of Wilson and Kern.

One remarkable feature of the results of Thomas and Baldwin is that when the logarithm of the concentration of hydrogen ion is plotted against concentration of added salt in the case of the alkali chlorides, the curves are apparently straight lines, of the general formula—

$$\log [H^+] = \log a + bm \quad (1)$$

where b is a constant, a the hydrogen-ion concentration with no added salt, and $[H^+]$ the hydrogen-ion concentration in the presence of m moles per litre of added salt.

Since all that remained to make this equation a valuable instrument for the rapid estimation and control of the hydrogen-ion concentrations of pickle liquors was the determination of b for various strengths of acid, the writer, assisted by Mr. Rudolph Olson, repeated the work of Thomas and Baldwin for other strengths of sulphuric acid and sodium chloride, using the same method and type of apparatus which they describe, excepting for the substitution of a Leeds & Northrup potentiometer for the Wolff bridge. The temperature, which was not controlled, varied between 18 and 22°. Our results for N, 0.1/N, and 0.025/N sulphuric acid, together with those of Thomas and Baldwin for 0.0005/N acid, are shown in Table I. and Fig. 1.

Table I.—Effect of NaCl Upon Hydrogen-Ion Concentration of Solutions of Sulphuric Acid.

Moles NaCl per litre.	Log [H ⁺] of N-H ₂ SO ₄ .	Log [H ⁺] of 0.1 N-H ₂ SO ₄ .	Log [H ⁺] of 0.025 N-H ₂ SO ₄ .	Log [H ⁺] of 0.0005 N-H ₂ SO ₄ .
0.000	—0.36	—1.22	—1.72	—3.50
0.428	—	—1.13	—1.62	—
0.856	—	—1.04	—1.56	—
1.000	—0.15	—	—	—3.29
1.284	—	—0.96	—1.45	—
1.712	—	—0.87	—1.37	—
2.000	+0.03	—	—	—3.10
2.140	—	—0.77	—1.27	—
3.000	+0.24	—	—	—2.92
3.210	—	—0.55	—1.05	—
4.000	+0.45	—	—	—2.71

Value of b 0.20 0.21 0.21 0.20

Apparently the curves are not only straight lines, but all four have the same slope, the average value for b being 0.205. The large percentage increase in hydrogen ion concentration upon the addition of 4 moles per litre of sodium chloride and the fact that it is practically the same, about 560 per cent, for widely different strengths of acid, suggest that the effect must be due to some action of the salt upon the solvent, such as hydration. It is of course apparent that any increase in concentration of acid caused by hydration of the salt will result in a lesser percentage ionisation of the acid, but at least 2 factors, other than hydration of the salt, will tend to cause an increase in hydrogen ion concentration, and these are the hydration of the acid itself and the fact that with increasing salt concentration there will be less total water, free and combined, per litre of solution. If these opposing tendencies exactly balance each other, that is, if they operate so that the percentage increase in hydrogen ion concentration found is equal to the percentage increase in concentration of total acid, then it is

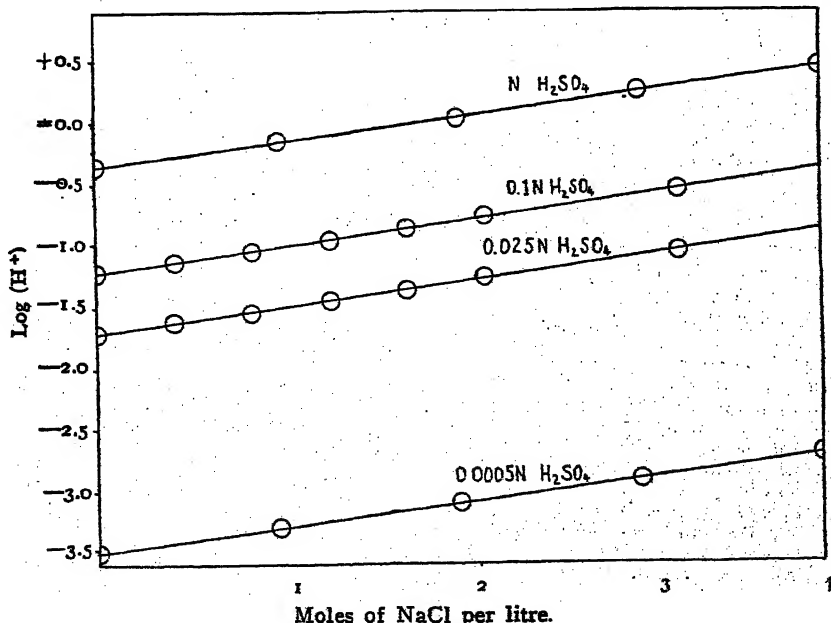


Fig. 1.

an easy matter to calculate the degree of hydration of the salt for any concentration. The fact that we get the same slope for all 4 curves seems to show that here the opposing tendencies are nearly balanced. Nevertheless, this may not prove true for other cases, so the safer plan would be to select acid solution so dilute as to make these opposing tendencies of negligible magnitude. It would appear, however, in the case of sulphuric acid, that $b=0.205$ for sodium chloride in all concentrations of acid less than normal. Let us, therefore, calculate the degree of hydration of salt in a solution of acid so dilute that we may neglect the hydration of the acid and its partial volume and consider it totally ionised.

From Equation 1 $\log ([H^+]/a) = bm$. But $[H^+]/a$ is the factor by which the acid concentration has been multiplied by adding m moles per litre of salt. Let w represent the total number of moles of water, free or combined with salt, in one litre of solution containing m moles of salt. The moles of free water then equal $wa/[H^+]$ and the moles of water combined with one mole of salt equal $(w/m) \times (1 - a/[H^+])$. Calling this latter value h , we have—

$$h = w(1 - 10^{-bm})/m. \quad (2)$$

Substituting 0.205 for b in Equation 2, we have calculated the degree of hydration of sodium chloride for several concentrations. (See Table II.).

Table II.—Calculated Values for Degree of Hydration of NaCl at Different Concentrations.

Moles NaCl per litre. (m).	Total moles water per litre. (w).	Molecules water combined with one molecule of NaCl. (h).
4.0	51.1	10.9
3.0	52.3	13.2
2.0	53.5	16.3
1.0	54.6	20.5
0.1	55.4	25.5
0.01	55.5	26.1
0.001	55.5	26.2
0.000	55.5	26.2

The striking agreement between our value of 26.2 for infinite dilution and Smith's (*Journ. Am. Chem. Soc.*, 1915, xxxvii, 722) calculated value of 26.5 by quite another method confirms the idea that hydration of the salt is responsible for the increase in hydrogen-ion concentration noted.

When it is required to calculate the degree of hydration only for infinite dilution, Equation 2 may be greatly simplified, since

$$\lim_{m \rightarrow 0} h = w(10^{bm} - 1)/m = 2.30wb = 128b. \quad (3)$$

Conversely, given the degree of hydration at infinite dilution, one may simply divide by 128 to get b and substitute in Equation 2 to calculate hydration values for any finite concentrations, provided of course the degree of hydration follows the rule expressed by Equation 2.

For the sake of comparison we made a set of determinations with N sulphuric acid and potassium chloride, the results of which are given in Table III. Since $b=0.14$, the degree of hydration at infinite dilution would be 128 times as great, or 18, which is not far from Smith's value of 19.2.

Table III.—Effect of KCl Upon Hydrogen Ion Concentration of N Sulphuric Acid.

Moles KCl per litre.	Log $[H^+]$.
0.0	—0.36
1.0	—0.21
2.0	—0.09
3.0	+0.05

Value of b 0.14

Thomas and Baldwin's results with hydrochloric acid show greater slopes for the alkali chlorides in 0.004/N than in 0.1/N acid. For each salt the value of b is less in the stronger solution by about 15 per cent of its value in the weaker one. Since complications introduced by the acid would naturally be less noticeable in more dilute solutions, the values of b in the weaker acid may be taken as more nearly representing the true index of hydration of the salts. Values for 128 b in 0.004/N hydrochloric acid follow: potassium chloride, 15; ammonium chloride, 15; sodium chloride, 26; lithium chloride, 35; and barium chloride, 50. Smith's corresponding values are potassium chloride, 19.2; ammonium chloride, 20.3; sodium chloride, 26.5; and lithium chloride, 33.6. Considering the limits of accuracy of the method as employed, the fact that temperature was not controlled, and that hydration of the acid and the repression of its ionisation were ignored, the similarity between these 2 sets of results seems more than a coincidence. In fact, the writer believes it strongly confirms, for chlorides, the earlier view that the neutral salt effect is due to hydration and also the suggestion that the Hofmeister series of the ions owes its nearly fixed order to the fact that the degree of hydration of the ions runs in the same order (*J. Am. Leather Chem. Assoc.*, 1918, xiii, 179).

The peculiar behaviour of the sulphates of sodium and ammonium in lowering the hydrogen-ion concentration of acid solutions, when one might have expected them to raise it very materially, may after all be found to be due to the same forces as bring about hydration. Their action can hardly be simply that of repressing the ionisation of the acid because of their effect upon chrome liquors, whose resistance to precipitation by alkalis they increase very much more than chlorides do, and this in view of the fact that in some cases they lower the hydrogen-ion concentration to a point at which precipitation of basic chromic salts might be expected without any addition of alkali. The tendency of sulphates to form additional compounds may eventually afford an explanation.

The nearly quantitative agreement between hydration values of the alkali chlorides at infinite dilution given by Smith and those calculated in this paper from hydrogen-ion measurements seems to warrant a much more extensive pursuit of the subject and especially of the use of the electro-metric method for studying hydration and its effect upon concentrated solutions.—*Journal of the American Chemical Society*, April, 1920.

RESULTS ACHIEVED IN INDUSTRY BY MODERN METHODS.*

By J. F. BUTTERWORTH.

(Concluded from p. 71).

Mr. L. M. COOKE, of Philadelphia, has stated that a standard under modern scientific management is simply a carefully thought-out method of performing a function or carefully drawn specifications covering an implement or some article of stores or of product. The idea of perfection is not involved in standardisation. The standard method of doing anything is simply the best method that can be devised at the time that the standard is drawn. Standardisation practised in this way is a constant invitation to further experiment and improvement.

This experimentation and improvement is done by time and motion study (*i.e.*, the study of the body's or machine movements) before the standards are made; thus the resulting standard is in so far protected that only the invention of a new device will make the change in such standard necessary. Standards have been advanced by a mere timing of the operation by mental counting. To do this silently, say to yourself, "And-one, And-two, And-three," and so on. Checked by a watch, you will find that three seconds have elapsed during a count by this method. Good work has been done by stopwatches, but where exactness, precision and a permanent record are necessary, micro-motion studies, elaborated by Major Frank Gilbreth, of which I will show examples presently, give the best results.

In practice it has also been found that such studies bring out many hitherto unsuspected defects in surrounding conditions, most of which are beyond the power of the worker to change, but which enable the management to eliminate many drawbacks, and thus increase efficiency and output. In one case I have heard of, a drilling machine was fitted with a claw-operated heavy jig; the machine had high-speed drills and was not suitably speeded, and the 15-lb. parts to be dealt with were on the floor, entailing lifting up and putting down when finished. By a suitable re-arrangement of the machine and letting gravity deal with the parts, an increase of 120 per cent was gained with less effort to the operator.

In another case close observation and timing showed that a machine could be slightly accelerated, thus gaining $1\frac{1}{4}$ seconds in the cycle. This seemingly small improvement, when applied to a number of similar machines in use, amounted to a total of over 20,000 hours in the year—a truly remarkable and substantial economy. The savings indicated in the foregoing instances do not mean the reduction of employment, for alternatively two things might happen. Firstly, another country might discover the cheaper and faster method, thus causing us to lose the market; secondly, if all nations keep the faster method from being adopted costs will remain high and the article will remain a luxury.

We have illustrations of this in all trades. For instance, take boots. Until the past few decades most workers had to use clogs; their grandfathers

were probably barefooted, and it was only when elaborate boot-making machinery was invented that good boots were reduced to a price within the reach of all classes. Increased production here meant health and comfort to millions, and greatly augmented good and steady employment to scores of thousands.

Incentives, under scientific management, can be defined as inducements to the worker to increase his efficiency, and a stimulant to prevent indifference to the work. Under "stimulants" we can place pleasant and sanitary working conditions, good heating, cooling, lighting and ventilating, and the recognition of individuality under the record system. Under inducements, the knowledge that if a man works his best he will be benefiting himself, but not doing his fellow-worker an injustice. There are far more chances of promotion than under the old system, for the simple reason that there are far more executive posts to be filled. Finally, there is the important question of pay, with fewer working hours; for every man may earn abnormally high wages provided that he works faithfully according to instructions and completes a task that has been fairly determined by scientific—and in future I hope—psychological and physiological data.

Before starting new methods and going to the trouble and expense of subjecting them to an intensive study, it is advisable, where possible, to begin with a survey of the old existing conditions. Gilbreth says that such survey may consist of a written description, supplemented by all available data—such as drawings, sketches, photographs, &c.—for recording what exists, what is taking place, and the times taken over the operations. It will serve as an important basis for the necessary future comparisons, and show what improvements in time or method are to be aimed at. The difficulty in preparing such a survey is to set down correctly what does exist. There is great temptation, especially if it is being done by an interested party, to set down instead what ought to exist, what is hoped will exist, what is planned should exist, rather than what is actually there. Try it for yourselves.

When you return to your work set down, or get a competent substitute to do so, what actually occurs in your place during one typical half hour. Add to this drawings showing the "set-up" or "layout" of your work, and where each piece of working equipment is placed, &c. Where plans exist, use them as a basis, drawing in the small objects. You will find this most interesting and stimulating as an attempt to make a survey of your own working conditions and practice, and you can then review it intensively, and then begin to introduce motion study.

Motion study is the science of eliminating wastefulness resulting from unnecessary ill-directed and inefficient motions. There are no ravages going on in nature to-day that equal the hourly losses the whole world is suffering from as the result of the wastage of human energy. Wasted motions cause wasted effort and time, and one of the results is unnecessary fatigue, another prime cause of high costs. Time is our greatest asset, and to waste it is to squander our inheritance. To waste time and to suffer unnecessary fatigue simultaneously can be excused only by ignorance.

* A Paper read before the Midland Counties Section of the Institute of Brewing, March 18th, 1920.

Unnecessary fatigue exists if the worker is obviously unfitted to the work either mentally or physically, or if the work is of a character which is uninteresting or unsatisfactory to the worker. Or again if the work could be done seated but is done standing, or if the work is done all day long without change of posture where some change is possible. Any standing job that will not permit arrangements for sitting 20 minutes of most of the working hours needs investigating by methods of motion study. Evidence of unnecessary fatigue becomes apparent should the working conditions be unhealthy or considered so by the workers, or should there be poor lighting, poor ventilating, too little or too much heat, or an insufficient variation in the range of heating, for an even temperature constantly maintained is enervating and exhausting. Further, if the working equipment is uncomfortable, if there is no provision for rest intervals, or if the output decreases in quality or quantity, or in both, with no apparent cause, are also indications of this form of fatigue.

Unnecessary fatigue is the evil to be attacked. When we come to necessary fatigue we cannot proceed far without recourse to careful measured investigation. These always show that less fatigue is necessary to do the work than has been anticipated.

In the final analysis, whether the fatigue proves to be necessary or not, it must be eliminated or cured, that is, recovery periods must be instituted. There are two methods of fatigue elimination—one the short method of removing the cause, the other by supplying the remedies.

What is not generally recognised is the following physiological fact pointed out by Professor Amar: "The fatigue of the nervous system is in proportion to the number of motor impulses which it is obliged to furnish to the muscular system in order to cause the latter to function, and here we see why in certain kinds of work which do not require strength there is considerable nervous exhaustion, while fatigue soon makes its appearance." Professor A. F. Stanley Kent is also of opinion that "the seat of fatigue is rather on the nervous than on the muscular side." You must realise from the beginning that fatigue study is a necessary complement to motion study, and that the fatigue which is the outcome of the motion must never for a moment be forgotten.

For instance, a long motion may occupy no more time than a short motion, but the fatigue will be greater with the amount of the distance traversed, all things remaining the same. Motion economy also involves a consideration of delays, the reasons why they occur, and a reconstruction of the method to such an extent that avoidable delays are eliminated, and that unavoidable delays are made rest periods or otherwise utilised.

The great and important result of motion study will be the change in your mental attitude. Nobody can really appreciate the benefit of motion economy who has not made motion study in his own work-place upon his own work, for you will see your own work-place yourself, and all that you do, in a new light. All activity outside and away from work will have more significance, and, perhaps the most important of all, you will see, more and more each day, the underlying elements of likeness in all types of activity. Just as there are physical elements, so there are elements of skill.

You will come to distinguish between skill and mediocre activity or bungling activity, and to note that an expert in any line bears certain resemblances to experts in other lines.

Motions or experts in all activities are alike; all are smooth, all are graceful, all show decision without hesitation, and all produce that satisfaction in the spectator that they produce in the creator of the motion.

This science has many phases, and separate instructive lectures could be delivered on Motion Study—Time Study—Fatigue Study—The Adoption of Standards—Accurate Measurement—Motion Models—Functionalisation of the Staff—Thinking and Planning Departments—Accurate Cost Finding and Keeping, for where this ends the accountant should begin—A Rational System of Paying Wages—"Employment" Management—Motion Photography of Men and Machines—Welfare or Betterment Work—The Human Factor and the Application of Psychology and Physiology to its requirements; for not only must the workers be studied but also the managers and staffs—and finally, Teaching under Scientific Management.

The above is a formidable list, and even so, does not cover the whole ground.

I will now show you a series of pictures, taken by Major Frank B. Gilbreth. In the evolution of scientific management, motion study as elaborated by him, and his application of psychological laws to the workers, have become important items. The material already accumulated by him is enormous and constitutes an extremely valuable collection of records for educational purposes.

In all motion study you must first have your units to measure, then your methods of measuring, and finally, devices to measure quickly and cheaply. Measurement is indeed the foundation, the base line of scientific management.

Many may consider the apparatus he uses expensive and elaborate, but I wish to emphasise particularly the fact that such equipment is not necessary for preliminary study. In fact, to realise thoroughly the need of more accurate measurement, it is first necessary to devote much thought along the lines of motion economy, and to work without any equipment. To make accurate studies of operations being performed wrongly, is a waste of time, energy, and money.

If I have convinced at least some of you that scientific management is not, as some from honest ignorance think, a mere device to exploit the workers, but a real living force capable, when properly installed and handled, of conferring untold benefits on all concerned, I shall feel rewarded. I ask those who agree with me that a method has at last been discovered that will give every man a fair chance and render rate cutting, strikes, and lockouts unnecessary, to help the cause of the workers by getting as many people as possible to take an interest in it and apply its teachings. I cannot finish better than by quoting Professor Amar's dictum on Scientific Management: "Selection and order are in truth the characteristics of the new method, which will presently work an economic revolution to which no other can be compared. It is not purely mechanical, it does not turn a man into a soulless body, a blind and tireless force, it embraces all the data of physiology and psychology, of

which it alone is able to display the parallelism and the unfailing harmony. It would seem to have taken for its guide this saying of Montaigne's: 'It is not a body, it is not a soul that we are forming, it is a man, we must not make two of him.'

DISCUSSION.

The CHAIRMAN (Mr. G. R. Burdass) said they had listened with a great deal of pleasure to Mr. Butterworth's paper. He was interested to learn that the coopers were the only body of workers in breweries who had joined in the Industrial League Whitley Councils. He thought as time went on other trades would also take advantage of them.

Mr. J. F. WARWICK said that in America the effort was made to get the workman to produce as much as possible, largely by making him comfortable in his work. But it was not always easy to get the British workman to see that. He (the speaker) had often argued with stokers, and told them it did not pay them to waste coal because they really wasted a lot of energy on throwing on coal uselessly. But they soon forgot the lesson. Probably their minds were not trained to understand such matters. With regard to efficiency machines, if the coopers who had joined the Council, or the Americans could invent machines for producing staves of the exact fit to replace a defective one in any cask, it would be a great help to brewers. They could get new casks or new cases made by machinery, but no machines had yet been invented which would produce a new stave to fit the space left by the removal of the defective one from a cask under repairs. The lecturer's suggestions would probably be more applicable to chilling and bottling than to other parts of the brewing process. Many of us would be delighted to speed up output, but there are some folk in this country who do not want us to produce more beer. He thought the reason the men in breweries generally had not joined the Industrial Council was due to the circumstance that the employers were mostly in very close touch with their men, and therefore any additional association was unnecessary.

Mr. W. R. WILSON said there were not many disputes in the Brewing Industry. Works committees were, however, being formed, which would no doubt serve a useful purpose. He did not think the Brewing Industry was quite so open to improvement in these matters as the engineering or the building trade. Probably economical operations of the kind described were more particularly applied to bottling.

Mr. BUTTERWORTH suggested whether improvements could be effected in shovelling, of which there must be a great deal done in the brewery. The late Dr. Taylor when manager of the Bethlehem Steel Works, America, was struck by the fact that there was only one type of shovel in use for all purposes, whether for lifting coal, coke, sand, gravel or iron ore. He found that the maximum weight that a man could lift, without undue fatigue, was 21.5 lb., and he had the shovel blades altered accordingly. He had smaller blades made for coal or ore than for breeze. Finally, some thirteen different types of shovel were used in the works. The effect of the change was that in a given time the weight lifted per man per day went from 16 to 56 tons. Obviously, also, the tall men should be put to work where material had to be

lifted some little height. In some cases the individual could not work more than 58 per cent of his time; 42 per cent of rest being necessary. Consequently, at the steel works above mentioned, rest periods were regularly given. If they made a man rest 42 minutes in 100 minutes he would do three or four times the work in a day than if he was employed continuously. Dr. Taylor found that when a man lifted continuously more than 92 lb. at a time he was over-fatigued, and that weight was therefore made the limit, the pigs being cast at that maximum. When a man had carried five pigs he was made to sit down and rest for a rather longer time than he had been carrying. The man at piece work earned 70 per cent more wages per day; and whereas he formerly carried 12½ tons, he was able to handle 47½ tons, though he worked less than half time. Very similar experiments in trench digging in France during the war led to exactly the same results. By giving the men periodical rests, over three times the amount of work was done in a day, the rest periods were strictly enforced. Production in many industries was seriously reduced, because the men were worked too long without rest, and so were over-fatigued.

The CHAIRMAN, in moving a hearty vote of thanks to Mr. Butterworth, expressed the hope that on another occasion he would give them a lecture, making a special application of his methods to the brewing industry.

DE-WATERING OF SEWAGE SLUDGE.

AN important contribution on the knotty problem of effectively dealing with sewage sludge was made at the Royal Sanitary Institute Congress at the University of Birmingham recently by Mr. F. R. O'Shaughnessy, F.I.C., Consulting Chemist to the Birmingham Tame and Rea District Drainage Board. He is the Hon. Sec. of the Birmingham and Midland Section of the Society of Chemical Industry. Many chemical engineers were present.

The points made by Mr. O'Shaughnessy were: That the problem of dealing with the sewage sludge is the crux of the sewage problem; and that the liquid part of the sewage can be dealt with satisfactorily in a number of different ways. The goal to be aimed at is to produce a liquid sewage effluent in the one case and the final solid product from the sludge in the other case which shall both be inoffensive and shall be produced by inoffensive means at a reasonable cost.

It is pointed out that the sludge is difficult to deal with because it is offensive; and is a complex colloid very retentive of water. Apart from sludge pressing, disposal at sea, and burial in the ground, which methods are not universally applicable, there remains only treatment by biological decomposition. Destruction by heat is ruled out because of expense. The biological method is that in vogue at Birmingham and it is claimed that as this process has worked satisfactorily, dealing successfully with the refuse of about a million of people over a period of 8 years, and that the cost has been an economical one, the process has justified its existence. Further the perennial nuisance attaching to all previous methods has been eliminated since its adoption.

Briefly, the Birmingham Sludge Digestion Process consists in promoting "septic" fermentation in chambers which are entirely separated from the chambers in which the crude sludge is collected. The process is carried on in such a way that no offensive gases come from the digestion chamber until the colloidal character of the sludge is largely destroyed. When the digestion is complete the sludge is pumped on shallow ash beds where it readily parts with its water without offence.

The crude sludge containing about 90 per cent water, dealt with by this process is close on 500,000 cube yards per annum, and the amount of solid matter destroyed in the process is over 30 per cent of the dry solid matter.

Mr. J. D. Watson, a well-known authority on sewage disposal, stated that the de-watering of sewage sludge was the best method yet tried for an inland centre, and he congratulated Mr. O'Shaughnessy upon his contribution.

SPONTANEOUS EVAPORATION.

By HARRY B. WEISER and EVERETT E. PORTER.

MORE than sixty years ago Babington carried out some interesting experiments on the spontaneous evaporation of salt solutions. An abstract (*Proc. Roy. Soc.*, 1859, x., 132) of this work was called to our attention by Professor Bancroft. "The object of this communication," says Babington, "is to make known certain powers of attraction and repulsion, hitherto, so far as I know, unnoticed, which are possessed by soluble substances in relation to their solvent, and which, in the case of water (the solvent here considered) are measured by the amount of loss, on spontaneous evaporation, in the weight of solution of different salts and other substances, as compared with the loss of weight of water.

"The force which holds together the particles of the vaporisable liquid is gradually overcome, if that liquid be exposed to air, by another force which separates, expands, and diffuses those particles in the form of vapour; and this separation takes place, even at common temperature, so rapidly, provided the surface be sufficiently extensive, that an easy opportunity is offered of determining the loss of weight by a common balance."

The method of experimentation followed by Babington consisted in exposing to the atmosphere for a definite period, solutions of different salts and also pure water under like conditions of quantity and area, temperature, atmospheric moisture, and atmospheric pressure. As evaporating pans were employed, vessels of tinned copper 5 inches square and $\frac{1}{4}$ inch high. The solutions were weighed before and after exposure on a balance that was sensitive to a grain even with a weight of 4 pounds on each pan. From a study of the rate of evaporation of a number of salt solutions he arrived at the following conclusions: "(1) That in any aqueous solution of salts and other soluble substances evaporation is retarded, as compared with the evaporation of water. (2) That in solution of salts which retard evaporation that retardation is in proportion to the quantity of the salt held in solution. (3) That different salts and other substances soluble in water have

different degrees of power in retarding its evaporation. (4) That the power of retarding evaporation does not depend on the specific gravity of a solution. (5) That in aqueous solutions of salts, the power of retardation does not depend on the base, whether we compare solutions containing like weights of the salt, or solutions of like specific gravities. (6) That in aqueous solutions of salts, the power of retarding evaporation does not appear to depend upon the salt radical or acid, although the retardation is not altogether independent of the influence of the base. (7) That salts with two equivalents of an acid have a greater power of retarding evaporation than salts with one equivalent. There are, however, exceptions. (8) That there are some salts which, being dissolved in water, do not retard evaporation, and some salts which, so far from retarding, actually accelerate evaporation."

An investigation of the data submitted in support of the first seven conclusions, disclosed that for the most part his results were readily interpreted in the light of the modern theory of solutions. However, the accuracy of the eighth conclusion seemed questionable, namely, that certain salt solutions evaporate more rapidly than water. In support of it the following data were given: "The eighth proposition which seems extraordinary and even paradoxical is proved by an experiment in which saturated solutions of 1, ferrocyanate of potassa, 2, bitartrate of potassa, 3, sulphate of copper, 4, chlorate of potassa, and 5, distilled water, were compared. In 9 hours and 20 minutes, their losses by evaporation were, respectively, 34 grs., 38 grs., 29 grs., and 29 grs., where we perceive that in the chlorate of potassa solution there has occurred no retardation at all, while in the following experiment, in which 120 grains of each of the salts examined were dissolved in 1200 grains of water, namely, 1, solution of sulphate of copper; 2, solution of ferrocyanate of potassa; 3, solution of carbonate of soda; and 4, distilled water; the number of grains lost by evaporation after 15½ hours' exposure were: 1, 120 grains; 2, 113 grains; 3, 106 grains; 4, 103 grains. It is thus perceived that in all three solutions a more rapid evaporation had taken place than in distilled water alone."

Since Babington's experiments apparently were carried out with considerable care we were not at first inclined to question their accuracy. Granting that the atmospheric conditions under which the evaporation took place were constant, the most obvious explanation of the higher rate of evaporation of certain salt solutions than of pure water seemed to be that the temperature of the solutions became higher than the solvent during the evaporation. In order to bring about the observed results, this temperature difference would have to be great enough to overcome the lowering of the vapour pressure of water by the dissolved solute. A difference in temperature between the solutions and the water might result from the heat of precipitation (in the case of saturated solutions) and the change in concentration, dissociation, and hydration occasioned by evaporation of the solvent. Calculation of the maximum heat energy available from the above sources under the conditions of Babington's experiments disclosed that the effect on the temperature of the solutions was so slight relatively and was spread over such a

long period of time that it was entirely negligible compared to the errors in weighing. A series of experiments were, therefore, carried out to determine the accuracy of Babington's observations.

Experimental.

At the outset we were convinced that there was nothing to be gained by working with a large volume of solution and weighing with approximate accuracy. Accordingly 2-inch crystallising dishes were used as containers for 10 cc. portions of the several solutions which were weighed on a sensitive balance. To prevent evaporation of the solutions during the weighing periods, the edge of each container was carefully ground and fitted with a ground glass plate. Before carrying out the earlier experiments the inside of the dishes was given a thin coat of paraffin to guard against "creeping" of the solutions; this was later discontinued since it was found that, in general, the rate of evaporation was more uniform from dishes that were not paraffined. The first evaporations were carried out on a stationary platform in the centre of a room ten feet square. The dishes were set the same distance apart on the circumference of a circle of 10-inch radius. It was hoped to secure uniform exposure in this way; but the results were not entirely satisfactory and a rotating platform was later employed as subsequently described.

The first experiments were carried out with salt solutions containing 10 grms. of salt per 100 cubic centimetres which was the concentration used by Babington. Ten cubic centimetres of each were placed in dishes which were arranged on a stationary platform as above described. The loss on evaporation was determined in a series of experiments, the results of which are given in Table I.

TABLE I.

Evaporation from a Stationary Platform.

	Loss on evaporation in grms.				
	I 20 hrs.	II 24 hrs.	III 16 hrs.	IV 18 hrs.	V 12 hrs.
Water	1.569	1.269	0.446	0.658	0.973
Water	1.586	1.278	0.419	0.653	0.963
Water	1.609	1.311	0.414	0.684	0.943
Copper sulphate	1.540	1.235	0.411	0.620	—
Pot. ferrocyanide	1.539	1.216	0.391	0.597	—
Pot. bicarbonate	1.495	1.202	0.380	0.624	—
Pot. nitrate ...	1.441	—	—	0.563	—
Pot. tartrate ...	1.441	1.132	—	0.555	—
Pot. carbonate ...	—	1.057	—	0.488	—
Pot. sulphate ...	1.390	1.135	—	0.568	—
Sodium carbonate	1.327	1.022	—	0.509	—
Pot. chloride ...	1.318	0.974	0.3235	0.481	—
Sodium chloride	1.309	0.897	0.2415	0.432	—

From the above table it will be seen that, contrary to Babington's observations, all solutions evaporated more slowly than water. However, the results are not entirely satisfactory as different samples of the pure solvent showed considerable variation in the rate of evaporation. Moreover, if the 10 per cent salt solutions are arranged in the order of evaporation rate, this order is not always the same. Such a variation can be due only to experimental errors. The most likely source of error seemed to be the failure to get uniform conditions of exposure. To obviate this it was decided to carry out the evaporations on a rotating disk that was 16 inches in diameter. This disk was turned once every half minute by

means of an electric motor geared down by the mechanism of an old Edison phonograph. The conditions of exposure were evidently much more uniform, as shown by the uniformity of the results given in Table II. In this experiment 6 samples of pure water were arranged the same distance apart on the edge of the circular platform which was rotated during the entire period of exposure. The loss in weight in 2½ hours, 5 hours, 10 hours, and 20 hours was determined.

TABLE II.

Evaporation of Water from Rotating Platform.

Sample	2½ hours	Loss in weight in 5 hours	10 hours	20 hours
1	0.234	0.509	1.039	1.716
2	0.238	0.519	1.053	1.743
3	0.237	0.514	1.042	1.721
4	0.235	0.510	1.044	1.724
5	0.236	0.513	1.041	1.725
6	0.232	0.506	1.032	1.711

As the above table shows the rate of evaporation was almost the same from each container. Accordingly, the rotating platform was used throughout all the subsequent experiments.

For the purpose of determining whether there was any advantage in using paraffined dishes, the rate of evaporation of water and of 10 per cent copper sulphate was determined, using both paraffined dishes and dishes thoroughly cleaned with hot chromic acid. The results are given in Table III. The time of exposure was 15 hours.

TABLE III.

The Effect of the Nature of the Container.

Sample	Loss in weight in Cleaned dishes	Paraffined dishes
Water	0.993	0.925
Water	0.994	0.925
Water	0.999	0.937
10 per cent Copper sulphate	0.962	0.903
10 per cent Copper sulphate	0.950	0.922
10 per cent Copper sulphate	0.962	0.898

The above results show two things; first, that 10 per cent copper sulphate evaporates more slowly than water instead of faster, as Babington found; and second, that a clean dish makes a better container than a paraffined one. The use of the latter is most likely to give erroneous results with saturated solutions, which tend to creep up the sides and deposit crystals if the dish is not thoroughly clean. This effect is shown in a striking way in the experiments recorded in Table IV.

TABLE IV.

No.	Sample	Loss on evaporation Grms.
I.	Water	0.917
	Saturated potassium sulphate	0.955
II.	Water	2.029
	Saturated potassium sulphate	2.342
III.	Water	1.805
	Saturated potassium chlorate	2.005

The above experiments might be considered to indicate that certain saturated solutions evaporate more rapidly than water. In every case, however, the solutions crept badly, depositing crystals on the sides of the dish. This increased the surface from which the evaporation took place and so the

results are not comparable. It is altogether probable that Babington's failure to take this into account resulted in the erroneous conclusion that certain saturated solutions evaporate as fast as, or faster, than the pure solvent.

From the above considerations it follows that if the saturated solutions do not creep during the process of evaporation, their rate of evaporation would be much smaller than the pure solvent. This is well illustrated in the experiments recorded in Table V. In this experiment particular care was taken to clean the containers and there was no creeping, so that all crystals deposited on the bottom of the dish instead of on the sides. Under these conditions the solutions evaporated much slower than water as the results show. It is interesting to note that the solutions used were the same as Babington found to evaporate more rapidly than water.

TABLE V.

Sample	Loss on evaporation Grms.
Water	0.735
Saturated potassium chlorate	0.669
Saturated copper sulphate	0.654
Saturated potassium ferrocyanide	0.617

A fairly accurate comparison of the relative lowering of the vapour pressure of water by different salts is obtained by comparing the loss on evaporation of solutions of suitable concentration. In the following experiment half-molar solutions of several salts were employed. The results are given in Table VI. In the first column the salts are arranged in the order in which they decrease the rate of evaporation, in the second is recorded the loss in weight after 14 hours' exposure; in the third, the approximate degree of ionisation, α determined from conductivity; and in the fourth, the approximate value of i (the ratio of the number of particles after dissociation to the number of particles before dissociation) calculated from the expression $i = 1 + (f - 1) \alpha$ where f is the number of parts into which a molecule dissociates.

TABLE VI.

Evaporation of Half-Normal Solutions of Salts.

Sample.	Loss on Evaporation Grms.	α	i
Water	0.735	—	—
M/2 Copper sulphate	0.696	23.8	1.24
M/2 Sodium chloride	0.679	74.3	1.74
M/2 Potassium chloride	0.675	79.9	1.80
M/2 Sodium carbonate	0.665	40.0	1.80
M/2 Potassium carbonate	0.633	60.0	2.20
M/2 Potassium sulphate	0.655	62.0	2.24
M/2 Potassium ferrocyanide	0.633	43.0	2.72

As the above results show the loss by evaporation of equimolecular solutions is least with salts that give the greatest number of ions, which is exactly what one might expect. The conformity of the results to the theory suggests the possibility of using the rate of evaporation as a means of determining the molecular weight of certain

dissolved solutes. The applicability of the method is limited, however, on account of the necessity of working always with fairly concentrated solutions and the experimental difficulties involved in securing and maintaining suitable conditions of exposure. That the rate of evaporation does give a good indication of the condition of a dissolved solute is emphasised by the following experiment:

Ostwald (*Zeit. phys. Chem.*, 1888, ii., 78) has shown that when CrO_3 is dissolved in water there is formed dichromic acid, $\text{H}_2\text{Cr}_2\text{O}_7$, instead of chromic acid, H_2CrO_4 , as might be expected from analogy with the action of SO_3 and water. To verify this, two solutions of CrO_3 in water were prepared: the first contained 1 mole of CrO_3 per litre; and the second one-half mole of CrO_3 per litre. The rate of evaporation of these two solutions was compared with the rate of evaporation of M/2 sulphuric acid. The time of exposure was 14 hours. The results are given in Table VII.

TABLE VII.

Sample.	Loss on evaporation. Grms.		
	1	2	Mean.
Water	1.149	—	1.149
M/2 Sulphuric acid	1.071	1.070	1.071
M Chromic anhydride	1.062	1.057	1.060
M/2 Chromic anhydride	1.094	1.113	1.104

From the above results it is evident that molar CrO_3 which corresponds to M/2 $\text{H}_2\text{Cr}_2\text{O}_7$ evaporates at almost the same rate as M/2 H_2SO_4 ; while half-molar CrO_3 , which would correspond to M/2 H_2CrO_4 , evaporates considerably faster than M/2 H_2SO_4 , showing that it is not M/2 H_2CrO_4 but M/4 $\text{H}_2\text{Cr}_2\text{O}_7$. This confirms Ostwald's conclusion that CrO_3 reacts with water to form chiefly dichromic acid rather than chromic acid. The fact that M/2 sulphuric acid evaporates somewhat faster than the same concentration of dichromic acid is due to the fact that the degree of ionisation of the latter is greater than the former in M/2 solutions (Walden, *Zeit. phys. Chem.*, 1888, ii., 71).

From the above series of experiments it is proven that Babington's conclusion is erroneous, namely, that certain salt solutions evaporate more rapidly than water under constant conditions of exposure at ordinary temperature and pressure. As has been shown, the chief source of error in Babington's work probably is the failure to maintain constant conditions of exposure. The factor which is most difficult to maintain constant is the extent of surface exposed, particularly if the containers are not uniformly clean. This source of error is magnified with saturated solutions which will creep badly if the sides of the container are not thoroughly clean. By carrying out the evaporations with clean glass containers on a rotating platform results can be duplicated consistently to within 1 per cent. All the results obtained under these conditions are readily explained in terms of the modern theory of solutions.—*Journal of Physical Chemistry*, May, 1920.

CORRESPONDENCE.

VALENCY AND IONISATION.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS of October 11, 1918, cxvii., p. 319, an article of mine appeared on Valency. Recently I have seen a criticism directed against the idea, of what might be termed a "crystal molecule."

So far as I am able to judge, the ideas advanced in my article are in agreement with certain parts of Langmuir's atomic theory; and Prof. Bragg in *Nature*, July 22, 1920, speaks of the diamond as a vast molecule.

The idea that atoms become in a sense ionised in solids, crystals in particular—because the evidence by means of X-rays gives direct support to the idea—is a very beautiful one, and it is one of the salient points in Langmuir's theory. This may remind the readers of the CHEMICAL NEWS of my definition of cohesion (and valency) on p. 320 (*loc. cit.*).

My object in writing is to point out that the ideas I have brought together are worthy of fresh perusal in the light of Langmuir's 1919-20 theory (I say this, as I am not claiming anything as my own), since every idea, as small as it may seem in itself, is a step in advance if it leads in the right direction. See also, Langmuir, CHEMICAL NEWS, July 16, 1920, p. 29.—I am, &c.,

F. H. LORING.

NOTES.

IRON AND STEEL INSTITUTE.—*Autumn Meeting*, 1920.—The Autumn Meeting will be held in Cardiff, at the South Wales Institute of Engineers, on September 21 to 24. The following is a list of the papers which it is expected will be submitted at the meeting:—

- E. D. Campbell and B. A. Soule: "Notes as to Rates of Reaction in Certain Steels at 930° C."
- C. G. Carlisle: "Electric Steels."
- W. Dixon: "The Electrification of the Works and Collieries of the Ebbw Vale Steel, Iron and Coal Co., Ltd."
- R. H. Greaves and J. J. A. Jones: "Temper Brittleness of Nickel-Chromium Steels."
- D. Hanson and Mrs. Hilda E. Hanson: "The Constitution of Nickel-Iron Alloys."
- W. W. Hollings: "Variations in the Heat Supplied to the Blast Furnace, and their effect on the Fuel Consumption."
- K. Honda and T. Murakami: "Graphitisation in Iron-Carbon Alloys."
- K. Honda and S. Saito: "On the Formation of Spheroidal Cementite."
- A. Hutchinson and E. Bury: "The Rough Cleaning of Blast-Furnace Gas at Skinninggrove by the Lodge Electrostatic Process."
- A. McWilliam: "Indian Iron Making at Mirjati, Chota Nagpur."
- W. Rosenhain and D. Hanson: "Inter-Crystalline Fracture in Mild Steel."

E. Schneider: "An Investigation of Various Forging Operations carried out under Hydraulic Presses."

J. H. Whiteley: "Experiments on the Deoxidation of Steel with Hydrogen."

Arrangements have been made for excursions to several works, &c., in the district. Further particulars can be obtained from Mr. G. C. LLOYD, Secretary, 28, Victoria Street, S.W.1.

CITY AND GUILDS OF LONDON INSTITUTE.—The Council have awarded diplomas of "Associate" to the following students who completed a full course of instruction at the close of the recent session:—Allen, R. H., Ascanio, W. de, Ayerst, W. G., Baillie, R., Baines, T. N., Bedford, L. H., Beresford, D., Bishop, H., Budgett, F. la T., Blair, T. S., Bowden, W. A., Buckell, J. H. W., Burkitt, S. T., Butler, F. W., Carter, R. H., Chapman, A. R., Chilton, O. H., Clifford, S., Coombes, L. P., Cousinery, E. de, Cowie, G. C., Cramer, W., Cronin, H. F., Cushny, J., Davis, G. W., Davis, J. S., Day, A., Dean, A. J., Dovaston, G. E., Dovaston, W. A., Downes, E., Edmunds, F. T. (Henrici Medal), Falkner, V. M., Fenton, J. M., Firnberg, L. B., Fraser, R., Gabel, R., Glasspoole, G. H., Goodman, R. T. W., Gordon, L. V., Gowing, H. J., Green, E. R., Grose, J. W., Hall, T. F. B., Harris, H. A., Hasselt, M. Van, Haward, F. B., Heading, F. R., Highett, R. F., Hills, B. A. C., Hinton, L. T., Hodge, H. W., Holley, E. G. (Siemens Medal), Holstrom, J. E., Hurley, T. F., James, R. T., Johns, J. P., Jones, E. M. R., Jones, E. R., King, G. B., Lee, W. Y., Lobjoit, W. H., Macculloch, A., Macgregor, J. C., Macqueen, E. N., Martin, G. W., Maughan, J. D., May, A. E., McLeod, R. C., McVie, A., Mooney, A. McL., Morphy, D. W., Moul, F. D., Nachshen, M., Naish, H. F., Naylor, E. J., Paget, A. L., Pearlman, A., Peters, H., Pomary y Tenaud, P. L., Ringang, R. D., Robins, B. G., Rowell, K., Ryves, F. D. M., Shipman, E. M., Sich, W. E., Simonson, W. F. (Bramwell Medal), Stavridi, A., Stern, M., Stevens, S. G., Sturt, C. G., Swann, A. H., Townshend, B. W. O., Turner, E. H., Tutleman, B., Vereker, H. C., Webster, E. H., Whyte, D., Wilson-Jones, R. A., Wood, L. J.

ASSOCIATED SCIENTIFIC AND TECHNICAL SOCIETIES OF SOUTH AFRICA.—A movement which has been proceeding actively for some time in Johannesburg, writes H.M. Senior Trade Commissioner in South Africa recently, culminated in the formation of a body to be known as the Associated Scientific and Technical Societies of South Africa. The new organisation will bring together eight or ten of the chief technical societies of South Africa into a common institution. The necessary funds are being obtained by a loan from the Chamber of Mines, by contributions from the capital funds of each society, and by an appeal to each of their members.

TREATMENT OF OVERSEAS AGENTS IN THE DOMINIONS.—During the difficult times that accompanied and have followed the war, United Kingdom manufacturers and merchants have no doubt received many complaints from their customers and agents all over the Empire. Many of these complaints are due to causes over which

firms here have no control, but one that is frequently made might, it is felt, to some extent be remedied, and that is, failure to notify agents and customers of the state of affairs in the industry at home, of ability to supply, of failure to execute orders, and of the reasons for such failure. Statements have been received from a number of agents, either direct or through His Majesty's Trade Commissioners, to the effect that not only do their principals not volunteer information as to the reasons for high prices and late deliveries, but that when asked for reasons which the agents can advance to their customers, their principals either ignore the request or reply in a brief and entirely unsatisfactory letter. An instance may be cited of a firm in one of the Dominions who took a great deal of trouble to secure a municipal contract and were assured that, if the goods could be delivered, the contract would be given to them. They cabled and wrote, but received no reply from their principals, who thereby jeopardised not only their own position with respect to further orders from that municipality, but also that of all the other firms represented by that agent. On the other hand, goods sometimes arrive almost before the agents know that they are coming at all. Overseas agents realise a good deal of the difficulties which exist at home and are prepared to take them into account. His Majesty's Trade Commissioners also lose no opportunity of meeting criticisms in this way, but it is felt that this plea does not altogether meet the case, and that irritation is sometimes caused which could be avoided, and which must be detrimental to the strong desire to purchase British goods which undoubtedly exists throughout the Empire. It is pointed out that manufacturers should remember that it is their agents, and not they, who have to live alongside and endeavour to do business with disappointed customers, and that failure to keep the agent properly informed may lead to the latter going to useless trouble and expense in obtaining orders which cannot be executed. A little more information from home and a little clearer indication of the possibilities of doing business would go a long way towards smoothing matters, and would tend to remove the impression that in more important things also, overseas agents and customers are not receiving due consideration.

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3149.

EDITORIAL.

THE following papers have been received for publication, and will be inserted as soon as space permits:—

"On Sodium Phosphide." By E. Tomkinson and G. Barker. A preliminary account of the reaction under various conditions, the product, and its reaction with water. Received August 9.

"The Volumetric Methods for Estimating Tin." By J. G. F. Druce, M.Sc., A.I.C. The volumetric methods for estimating tin have been examined. The metal can be readily determined in acid solution by means of standard iodine solutions. Titration with permanganate gave satisfactory results in the presence of sulphuric acid. Received August 7.

"Polymerisation in the Solid State." By William R. Fielding. This paper, which is a continuation of "Aggregation at the Melting Point," commenced in CHEM. NEWS, cxx, No. 3136, p. 241, deals comprehensively with polymerism amongst the elements and the chief classes of compounds. A number of striking results are given. Received August 9.

ISOMERISM, TAUTOMERISM, AND PSEUDOMERISM OF ORGANIC COMPOUNDS AND THEIR RELATION.

By INGO W. D. HACKH.

THE purpose of this paper is the formulation of a system and classification of isomeric organic compounds which enables a clear cut distinct definition of the terms isomerism, tautomerism, metamerism, desmotropism, and pseudomerism. All these phenomena are caused by differences in the structure of the organic compound; they belong therefore to structural phenomena and their classification must be based upon their structural differences. While for practical reasons it may be advantageous to base a division of these cases upon dynamical grounds, that is upon the ability to transform one form into the other, it is nevertheless a question of structure.

There are six factors to consider, two of which (K and N) are self-evident and included to show the connection with polymerism, homologous and isologous series. The relation among these six factors and the corresponding category are shown in the following key to isomeric phenomena in which—

- N is the number of atoms in the organic molecule;
- K the kind of atom in the organic molecule;
- P the position or arrangement of atoms;
- T the chemical type of compound;
- V the valency of the principal atom,
- L the linkage or connections between the atoms.

The first group of cases—isology, homology, and polymerism—does not come properly under the heading of isomerism, but is related to it. The second group has as its characteristic the difference in the *position* of the atoms and is thus isomerism proper, with the subdivisions of structure isomerism, cis-trans isomerism, and stereo isomerism. The third group has as earmark a difference in the *type* of compound and is known as tautomerism in general, but may be divided into metamerism, desmotropism, and tautomerism. The fourth group is marked by a difference in the *valency* of the principal atom and is designated pseudomerism.

Isomerism needs no explanation or definition. It includes all the cases described as (a) chain isomerism (e.g., propane and isopropane); (b) place isomerism (e.g., 1-chloropropane and 2-chloropropane); (c) meta-isomerism (e.g., ∇ 1-butylene and ∇ 2-butylene or 3-pentanone, 2-pentanone, and 1-pentanone) which should not be mistaken for metamerism; (d) ring isomerism (the o-, m-, and p-, the v-, s-, a- positions); (e) side-chain isomerism (e.g., propylbenzene and isopropylbenzene); and (f) mixed isomerism (e.g., α -chlorotoluene and 2- or o- chlorotoluene). All these cases can be properly termed structure isomerism, for they are based on a different two-dimensional arrangement of the atoms in the organic molecule. In the second series of isomerism, sometimes called geometrical or cis-trans isomerism, there is a double bond either between (a) two carbon atoms, (b) two nitrogen atoms, or (c) a C and N atom. To this group belong all cis-trans forms of aliphatic and aromatic compounds as well as the syn- and anti-forms. In the third and last series of isomerism

Organic molecules or radicals show—

		K	N	P	T	V	L	
Isology	when d	s	—	—	—	—	(structure the same)
Homology	when s	d	—	—	—	—	(structure the same)
Polymerism	when s	d	—	—	—	—	(percentage the same)
Structure Isomerism	when s	s	d	—	—	—	—	(two-dimensional)
Cis-trans Isomerism	when s	s	d	—	—	—	—	(three-dim., inactive)
Stereo Isomerism	when s	s	d	—	—	—	(three-dim., active)
Metamerism	when s	s	d	d	s	s	
Desmotropism	when s	s	s	d	s	d	
Tautomerism	when s	s	d	d	s	d	
Pseudomerism	when s	s	—	—	d	—	

where s=same, d=different, and —=same or different.

there is an asymmetrical atom, which can be either C, N, Si, &c. All of these cases of isomerism are well known and a few examples will suffice. Fig. 1 shows some typical cases of isomerism represented by structure symbols.

(*Can. Chem. J.*, 1918, ii, 135; *Science*, N.S., 1918, xlviii., 333; *CHEMICAL NEWS*, 1919, cxviii., 289. Although it has been said that the structure symbols where a radical change from our conventional symbols, the writer must confess that he sees in the structure symbols nothing fundamentally new or deviating from the accepted theories, but merely a shorter and accurate device to represent structure formulæ which undoubtedly possesses some advantages, which will well repay the initial inconvenience of understanding and using these structure symbols).

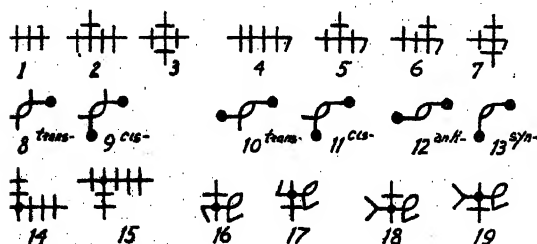


FIG. 1.

Examples of Isomerism.

a. Structure Isomerism:

Butane (1), isobutane (2), and tetramethylmethane (3). Propylcarbinol (4), isopropylcarbinol (5), methylethylcarbinol (6), and trimethylcarbinol (7).

b. Trans- Cis- Isomerism:

Trans- (8), and cis- (9) forms of $-\text{CH}=\text{CH}-$ radical. Trans- (10) and cis- (11) forms of $-\text{CH}=\text{N}-$ radical. Anti- (12), and syn- (13) forms of $-\text{N}=\text{N}-$ radical.

c. Stereo Isomerism:

Dextro- (14), and lævo- (15) methyl-ethyl-propyl-methane. Dextro- (16), and lævo- (17) lactic acid. Dextro- (18), and lævo- (19) alanine.

Tautomerism expresses itself in a difference in the type of compound, that is, the same number and kind of atoms in an organic molecule, which may or may not have the same relative position or linkage to each other, will by a change of position or linkage produce a different type of compound. To this class belong three categories: (a) metamerism, where the linkage remains the same, but the position is different; (b) desmotropism, where the position remains the same, but the linkage is different; and finally (c) tautomerism proper, where both, the position and linkage, is different. It is remarkable to find on examination of tautomeric cases that the majority belong to the desmotropic category, while the tautomeric category is comparatively rare. Desmotropism is a name little used, yet it describes aptly and excellently the phenomena as a "turn or change of the bonds or linkage" and thus characterises what actually happens. This turn or change is well illustrated in the structure symbols of Fig. 2, giving some examples of the three categories of tautomerism.

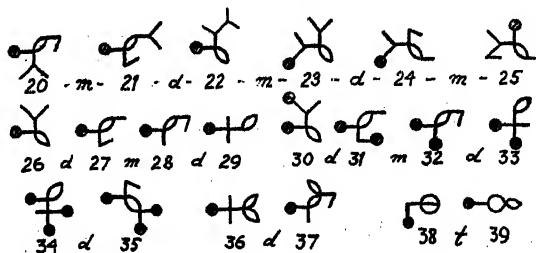


FIG. 2.

Examples of Tautomerism.

a. Metamerism:

$-\text{CH}_2\text{ON}_2$ = amidoximes (20) and hydrazone acids (21) acid hydrazides (22) and ureides (23). pseudo-ureides (24) and acid hydroxylimides (25). $-\text{CH}_2\text{ON}$ = acid imides (27) and oximes (28). $-\text{CHON}$ = imidoethers (31) and ketoximes (32).

b. Desmotropism:

$-\text{CH}_2\text{ON}_2$ = hydrazone acids (21) and acid hydrazides (22). ureides (23), and pseudo-ureides (24). $-\text{CH}_2\text{ON}$ = acid amides (26) and acid imides (27). oximes (28) and nitroso-methyl compds. (29). $-\text{CHON}$ = acid amides (30) and imidoethers (31). ketoximes (32) and nitroso-methylen compds (33). $-\text{C}_2\text{HO}_2$ = ketones (34), and enols (35). $-\text{CH}_2\text{NO}_2$ = nitro-compds. (36) and iso-nitro compds. (37).

c. Tautomerism:

$-\text{OCN}$ = cyanates (38) and isocyanates (39).

Pseudomerism involves a change of valency, and as there are relatively few cases of this type a further sub-division seems at present unnecessary. The more important cases are those of R-ONO and R-NO_2 , R-CN and R-NC , R-OCN , and R-ONC (R-OCN is tautomeric to R-NCO , but pseudomeric to R-ONC). Further examples are illustrated in Fig. 3.

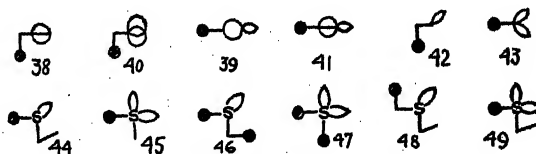


FIG. 3.

Examples of Pseudomerism.

$-\text{OCN}$ = cyanate (R-OCN , 38) and pseudocyanate (R-ONC , 40) isocyanate (R-NCO , 39) and pseudo-isocyanate (R-CNO , 41). $-\text{NO}_2$ = nitrite (R-ONO , 42) and nitro-compd. (R-NO_2). $-\text{SO}_2\text{H}$ = alpha (44) and beta (45) sulphonic acids. $=\text{SO}_2$ = alpha (46) and beta (47) sulphonous. $-\text{SO}_2\text{H}$ = sulphurous or alpha (48) and beta (49) sulphonous acids.

Isologous series are formed by compounds of a similar structure, but with different atoms. This definition restricts Gerhard's original conception of isologous series to a smaller group of compounds. Such a restriction seems justified and perhaps necessitated by the increase of knowledge which requires an ever-growing specialisation. Thus, e.g., isologues of pentacyclic compounds may be of the furan type $-\text{C}_4\text{H}_4\text{O}$, $\text{C}_4\text{H}_4\text{S}$, $\text{C}_4\text{H}_4\text{Se}$; or of the pyrrole type $-\text{C}_4\text{H}_4\text{NH}$, $\text{C}_4\text{H}_4\text{PH}$, $\text{C}_4\text{H}_4\text{AsH}$; or of the pentamethylen type $-\text{C}_4\text{H}_4\text{CH}_2$ ($=\text{C}_4\text{H}_4$), $\text{C}_4\text{H}_4\text{SiH}_2$, &c. Some examples of isologous series of types of compounds are given in Fig. 4.

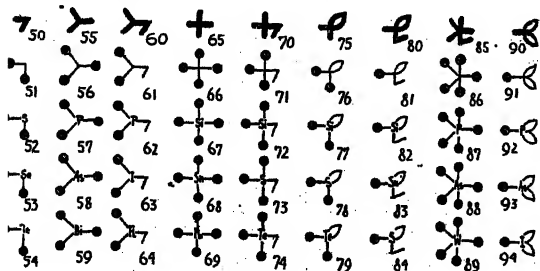


FIG. 4.

Examples of Isologous Series of Types.

- Isologues of water (50):
Oxides or ethers (51), sulphides (52), selenides (53), tellurides (54).
- Isologues of ammonia (55):
Tertiary amines (56), phosphines (57), arsines (58), bismuthines (59). Similar also Sb, I, B, Al, &c.
- Isologues of hydroxylamine (60):
Hydroximinines (61), hydroxylphosphines (62), iodonium hydroxides (63), thallium hydroxides (64).
- Isologues of methane (65):
R₄-methanes (66), silicanes (67), stannyles (68), plumbyles (69).
- Isologues of carbinol (70):
Tertiary alcohols (71), silicols (72), sulphines or sulphonium compounds (73), tellurionium compounds (74). Similar are also Sn, Pb, &c.
- Isologues of formaldehyde (75):
Ketones (76), silicon oxides (77), sulphoxides (78), tellurium oxides (79). Similar are Sn, Se, &c.
- Isologues of formic acid (80):
Acids (81), siliconic acids (82), stannonic acids (83), alpha sulphinic acids (84).
- Isologues of ammonium hydroxide (85):
Quaternary amines (86), phosphonium compounds (87), arsonium compounds (88), tungsten compounds (89). Isologues are astibonium compounds.
- Isologues of tauto-nitric acid (90):
Nitro compounds (91), phosphino compounds (92), arsino compounds (93), iodo compounds (94).

Homologous series and polymerism are too well known to need illustration, their characteristics are already mentioned in the key to isomeric phenomena.

San Francisco, Cal.,
College of Phys. and Surg.

AGGREGATION AT THE MELTING POINT.

By WILLIAM R. FIELDING, M.A., M.Sc. (Vict.),
Senior Science Master at King Edward VII. School, Lytham.

(Continued from vol. cxx., p. 255).

Last Portion of the Curve (beyond 932°).

OWING to the high melting points, the rapid changes in the values of specific heats (the specific heat of nickel rising from 0.0575 to 0.1338 between 100° and 900° and the specific heat of diamond from 0.0635 to 0.4589 between 223° and 1258°), the greater difficulty of measuring the higher melting points with exactness, and the greater possibility of experimental error, the calculated values of R, melticular weights, and specific heats at the melting point may not be so accurate as those previously obtained. The curve has been calculated from Al₈₈ and Fe₈₀. The latter value was obtained after frequent trial, e.g., the specific heat of Ag at 100° is 0.0467 and it rises to 0.0590

at 700° when it becomes almost constant. The formula from Al₈₈ and Fe₈₀ is

$$\frac{\text{M.P.} + 1683}{\sqrt{\text{Melticular weight}}} = 66.$$

$$\text{i.e., } \frac{\text{M.P.} + 1683}{66} = \sqrt{\text{Melticular weight.}}$$

The melticular weight of silver is therefore 1955, its R about 18, and s (at 1233.5° A, its M.P.) = 0.0603, not much different from the highest recorded value, viz., 0.059 at 700°. The value of R for nickel, however, is only 45.6, whereas the value required to give it its highest recorded specific heat (0.1338 at 900°) is 57; but this discrepancy need not be seriously entertained at present as one expects exceptional properties for nickel owing to its anomalous position in the periodic system. The equation obtained from Al₈₈ and Ni₈₇ is

$$\frac{\text{M.P.} + 798}{43.6} = \sqrt{\text{Melticular weight.}}$$

The mean of the two equations is

$$\frac{\text{M.P.} + 1240}{54.76} = \sqrt{\text{Melticular weight.}}$$

and this was used to find the data of all elements whose melting points are above 932°. These results are given in Table VIII. and the reader is asked to suspend judgment on the very high values for carbon, &c., until a later point in this paper.

TABLE VIII.

Section	Element	M.P.	Melticular Weight.	R.
I.	Helium	2°?	1	0.25
	Hydrogen	14°	12	12
	Neon	20°	18	0.9
	Fluorine	50°	57	3
	Oxygen	55°	66	4.1
	Nitrogen	63°	78	5.6
	Argon	85°	108	2.7
	Krypton	104°	138	1.66
	Xenon	133°	190	1.46
	Q (Thorium Emanatum)	153°		
II.	Chlorine	171°	248.5	7
	Hg	234.1°	347	1.74
	Br	266°	400	5
	Cs	299°	459	3.45
	Ga	303°	466	6.6
	Rb	311°	481	5.6
	P (yellow)	317°	493	16—
	K	335.3°	528	13.5—
	Na	370.5°	600	26
III.	I	386.7°	635	5
	S	385.8°	635—	10.8
	In	428°	691	6+
	Li	459°	735	104.5
	Se	490°+	780	9.84—10
	Sn	504.9°	802	6.75
	Bi	544°	862	4.1
	Tl	575°	914.4	4.5
	Cd	593.9°	942	8.38
	Pb	600.4°	952.5	4.6
	Zn	692.4°	1108	17
	Te	725°	1167.8	9
	Sb	903°	1512	12.5
	Ce	913°	1534	10.95
	Mg	924°	1555	63.85
	Al	932°	1573	58

Section Curve, Element	M.P.	Melting Weight.	R.
IV. Ra	973°	1631	7.25
Ca	1083°	1801	44.9
La	1083°	1801	13
Sr	>Ca < Ba	1830?	20.9
Nd	1113°?	1843	12.8
As	1123°	1858	24.8
Ba	1123°	1858	14.2
Pr	1213°	2005	14.2
Ge	1231°	2034	28
Ag	1233.5°	2037	19—
Au	1336°	2207	11.2
Cu	1356°	2245	35.3
Mn	1503°	2506	45.5
Be	1553°	2595	285
Sa	1573°—1673°	2731?	18?
Sc	?	2731?	62?
Si	1693°	2867	101
Ni	1725°	2927	50
Co	1753°	2982	50.5
Yt	1763°	3002	33.7
Fe	1803°	3083	55
Pd	1822°	3127	29.3
Cr	1888°	3262	62.6
Zr	1973°?	3445	38?
Nb	1973°?	3445?	36.6
Th	24 1973°?	3445?	14.8
V	1993°	3539	69
Yb	?	3600?	21?
Ti	2073°	3657	76
U	<2123°	3755	15.7
Rd	2223°	3991	38.7
B	2473°—2773°?	4909?	452?
Ir	2623°?	4909?	25.7
Ru	2723°	5235	51.4
Mo	2823°	5500	57.3
Os	2973°?	5914	31—
Ta	3173°	6489	35.4
W	3673°	8041	43.7
C	>3873°	8710	726

(To be continued).

ISOTOPISM.

By J. FREDERICK CORRIGAN.

TRUE science has always been rightly accredited with a supreme honesty of purpose, a desire for absolute Truth, and an almost unhuman faculty of freely admitting mistakes. "To reveal, not to conceal" has been its watchword. But the latter propensity of admitting mistakes and fallacies, errors of judgment, and mal-observations, and of even courting correction is only a comparative modern acquirement of science. Noble and grand as was the progress of the Victorian giants of science, they were only human, and they were apt to become irritable and lay down dogmatic assertions when any intruding foot crossed their paths of work. The Victorian man of science was nothing if not material and concrete. The vague utterings and mystical speculations of countless generations of ritualistic alchemists and other "adepts" had had their effect, and towards the end of the eighteenth century a new type of person was found coming into prominence; an individual who like the legendary youth, "held a banner with a strange device"—Experiment!

It is therefore not surprising that as the nineteenth century grew in years, certain ideas became fixed in the collective mind of science—ideas which were firmly rooted there simply because no attempt had been made to question them. And one of these fixed ideas was the Boyle-Dalton conception of the Element and the Atom.

Originally having its rise in ancient metaphysics, and centuries afterwards in empirical experiment, the conception of the Atom and the Element was raised to the pinnacle of supreme truth. The atom was regarded as an infinitely minute spherical body, and moreover it was *impenetrable*. Dalton really took Newton's hypothesis of the atom being a "solid, massy, hard, impenetrable" body, and gave to it a new significance which he developed into his atomic theory. And there the matter rested; it was final. The atom was regarded as being a fundamental and indivisible unit, and the existence of a state "beyond the atom" was undreamt of.

On the conception of the Atom and Element there was gradually built up a wonderful system of qualitative and quantitative analysis. It was considered that by the act of analysis, a compound was separated into its fundamental constituents, and that even by the most delicate methods imaginable the compound could not be "analysed" any further.

Founded on the fundamental idea of the element, a most remarkable classification of the known elements was gradually evolved. This table of elements, originated by the Englishman Newlands, and subsequently developed by Mendeléeff, has proved to be a wonderful stimulant for investigations into the relationship which certainly exists between the elements both in their free and combined state. Its true significance, however, still remains a mystery, and theories of the constitution of matter have been brought forward from time to time to explain it, but only to be found out of confirmation with the general facts. Still, however, the Daltonian idea of the elementary atom as a fundamental and ultimate unit held sway, practically unrestrained.

Crookes' Meta-Elements.—One of the first men to postulate that, whilst the atomic theory of matter was rational as far as it went, but that it did not go far enough, was the late Sir William Crookes. In 1887, Crookes was struck by the extreme closeness of the relationship between the rare earth metals, and he put forward the theory that these metals might possibly be modifications or variations of one parent element. He separated yttria into several different components, each possessing different phosphorescent spectra, but differing only minutely in chemical properties. The original yttrium was universally acknowledged to be a true element, having an unvarying atomic weight, and other definitely ascertained physical constants. Here there was an element which could be split up into a number of different parts each possessing different phosphorescent spectra, and yet having practically no chemical differences.

For these different constituents of an element, Crookes introduced the term *meta-elements*. The properties of an element were supposed to be the average of the properties of its constituent meta-elements, if any. Ordinary chemical analysis was able to separate the groups of meta-elements from

one another, but it was powerless to effect a separation of the meta-elements themselves.

The Evolution of the Theory of Isotopes.—Crookes' theory of meta-elements did not meet with much success. Those who upheld it were at least considered to be irrational, and even actually eccentric. The old idea of the element as an entirely "pure" and homogeneous body was too deeply rooted to be disturbed by this hypothesis. In fact, probably only Crookes himself saw that in our much-prided analysis, we are not dealing with "pure" elements, but only with types of elements. Consequently, the theory was disclaimed and over-ridden.

The discovery of radio-activity and the radio-active elements which occurred at the beginning of the present century forcibly brought home to chemists, and scientific philosophers generally, the necessity of revising their definitions of atoms and elements. Here, under their very eyes, was a body which satisfied all the demands made of an element, splitting itself up into other elements of lower atomic weight. This process of transmutation was as unaffected by any external conditions as it was ceaseless and unrelenting.

The varied phenomena of radio-activity demanded immediate explanation, and the first general and comprehensive theory saw the light in the form of Soddy's Theory of Atomic Disintegration. The old idea of the atom and element was retained, in fact the discovery of radio-activity rather strengthened the idea of the atom, but its conception was retained in a different light. From henceforth the atom, although it was the unit of chemical combination, was not the fundamental unit of matter. An atom might contain a lilliputian atomic system itself.

Soddy, by his theory of atomic disintegration, showed that during the spontaneous breaking down of a radioactive element, α , β , and γ rays may be given out. The rays were found to consist of a stream of positively charged particles of matter, an α particle being no less than an atom of helium associated with two positive charges of electricity. The β rays are composed of negatively charged corpuscles, having a mass equal to only $1/2000$ of the hydrogen atoms. The γ rays are considered to be similar, if not identical with the Röntgen or x rays. Their exact nature, however, is uncertain (Bragg, *Phil. Mag.*, 1910, vi., 20, 385).

At this point, however, it is necessary in order to obtain a clear impression of the development of the theory of isotopes, to turn for a moment to the theory of valency due to Abegg (*Zeit. Anorg. Chem.*, 1904, xxxix., 330). According to this theory, every element possesses two kinds of valency, a *normal* and a *contra* valency. These valencies are electrically different, the normal

valencies being positive in the metals, and negative in the case of the non-metals. The normal valency is usually the stronger of the two, and it corresponds to the generally accepted valency of the element, the contra valency being latent or dormant. According to Abegg, the sum of the normal and contra valencies is always eight, and is divided between the elements in the different groups of the periodic table, as shown in Table I.

It was discovered that when a radioactive atom disintegrates with the expulsion of an α particle, it loses four units in mass. It also loses two units of positive electricity, and therefore two units of valency. Consequently, the new atom appears in the periodic table two places for the left of the original element. Thus when Radium (group II.) of at. wt. 226 loses an α particle, the resulting atom (Niton) appears in Group 0, and has an atomic weight of 222.

If, however, an atom of a radioactive element loses a β particle, the mass of the resulting atom is to all practical intents and purposes not affected, but the positive charge of the atom is increased by one unit, and also the valency of the atom is increased by one. Thus the new atom finds a place in the periodic table one place to the right of the position occupied by the parent element.

In illustration of these views it will be interesting to follow the radioactive disintegration of the thorium atom. In this case, an α ray change occurs primarily, and is followed by two consecutive β ray changes. On the loss of an α particle by thorium, the new atom—*Mesothorium I.* appears in group II. of the periodic table and has an atomic weight of 228—four units lower than the atomic weight of thorium. On the expulsion of a β particle from mesothorium I., a new element—*Mesothorium II.* results. This possesses an atomic weight identical with meso-thorium I., and on the further expulsion of a β particle, an element is obtained—*Radio-thorium*—which although possessing an atomic weight four units lower than thorium, appears in the same group as the latter. (Table II). Elements, such as thorium and radiothorium, which although possessing different atomic weights, fall in the same group in the periodic table were called by Soddy "Isotopes" (*Isos*, equal; *topos*, a place).

As the mass of the β particle is negligible, it follows that the atomic weights of the new elements mesothorium II. and radiothorium will be identical with the atomic weight of mesothorium I. Thus in addition to the phenomenon of elements possessing different atomic weights, yet falling in the same group in the periodic table, we are confronted with the additional fact that it

Periodic Table Group.	I.	II.	III.	IV.	V.	VI.	VII.	0 (or VIII) Transitional Group.
Normal Valencies	+1	+2	+3	+4	-3	-2	-1	0
Contra Valencies	-7	-6	-5	-4	+5	+6	+7	0

TABLE I.—Illustrating Abegg's Theory of Valency.

is possible for elements to have the same atomic weight, and yet find places in different groups in

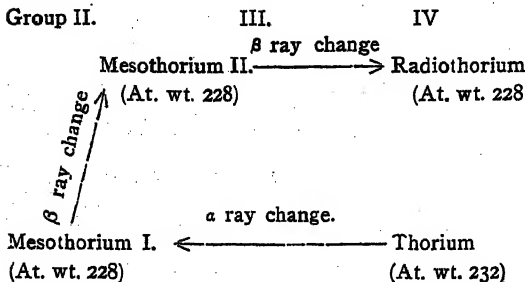


TABLE II.—Table illustrative of the terms
Isotope and *Isobar*.

the periodic table. For elements such as mesothorium II. and radiothorium, which although possessing similar atomic weights fall in different groups, the term "Isobars" (*Isos*, equal; *baros*, weight) has been suggested.

An entirely new idea was given to the world in these views. The homogeneity of the elements was beginning to be doubted, and what had formerly been considered to be a "pure" element might now prove to be a mixture of atoms possessing different atomic weights, but chemically inseparable.

A year or two later, the atomic weight of lead was determined by several investigators, and it was found to vary slightly according to the source of the mineral from which the lead was obtained (M. Curie, *Compt. Rend.*, 1914, clviii., 1676; Hönigschmid and Horovitz, *ibid.*, 1796). This variation in atomic weight was found to be between 206.40 and 207.15. Allowing for experimental error, it was at once apparent that ordinary lead was a mixture of two different kinds of lead which were more or less chemically inseparable.

The admirable work of Hönigschmid (*Monatsh.*, 1912, xxxiii., 253) on the atomic weight of radium was such that the atomic weight of the element was accurately known to be 226. Allowing for the expulsion of five α particles from radium, it became evident that the element formed would fall into the same group in the periodic table as lead, and would have an atomic weight of 226, thus differing by 1.1 from the generally accepted value for the atomic weight of lead. Thus it was shown that the element lead was not composed of atoms of the same atomic weight, but that it contained at least two sorts of atoms, chemically identical, and differing from each other in mass.

A third isotope of lead may also exist, for if allowances are made for the loss by thorium of six helium atoms, during its radioactive disintegration, the resultant element would find a place in the same group as lead, and would have an atomic weight of 208. Ordinary lead, therefore, is probably a mixture of three isotopes of atomic weight 206, 208, and 210, although according to some authorities, the end product of the disintegration of thorium is not lead, but bismuth.

(To be continued).

THE TRUE TANNING VALUE OF VEGETABLE TANNING MATERIALS.*

By JOHN ARTHUR WILSON and ERWIN J. KERN.

DURING the past century an enormous amount of energy has been expended in efforts to devise a method for determining the tannin content, or rather the true tanning value, of vegetable materials. Numerous methods have been proposed, but without any indication as to the correctness of the results obtained. (For a review of work done since 1803, see Procter's "Leather Industries' Laboratory Book" (Spon. 1908), pp. 168-176). In fact the methods now in general use, both here and in Europe, were made official without any knowledge as to their accuracy, but solely because they are of such nature that different analysts have comparatively little difficulty in concordant results. Since tanning materials are usually sold on a tannin basis, these methods have proved of very great value in enabling buyer and seller to agree as to price, but investigators who have blindly accepted the results as reliable have sometimes been led into serious error. In this paper we present what we believe to be the first successful method for determining the true tanning value of vegetable materials.

Practical Definition of Tanning.

Work on the chemistry of the tannins is still so far from complete that no rigid chemical definition of them as a class can be given, but their extensive use, especially in the leather industry, has necessitated defining them in terms of some property of practical value. It has therefore become customary to apply the name *tannin* to that portion of the water-soluble matter of certain vegetable materials which will precipitate gelatin from solution and which will form compounds with hide fibre which are resistant to washing. The remaining portion of the soluble matter is called *non-tannin*.

New Method.

Principle of the Method.—The method aims, of course, to determine exactly what is called for in the definition. A convenient amount of the tanning material is shaken with a definite amount of purified hide powder until all tannin has been removed from solution. This point is determined by filtering off a portion of the residual liquor and adding drop by drop, avoiding a large excess, a solution containing 10 grms. of gelatin and 100 grms. of sodium chloride per litre; if the solution becomes turbid or a precipitate forms, it shows that all tannin has not been removed from solution, in which case the mixture must be discarded and the test repeated, using less of the tanning material or shaking for a longer time, until the solution after filtration gives no visible reaction with the gelatin-salt reagent. The tanned powder is then washed free from soluble matter, including the non-tannin removed from solution by the hide powder, which is responsible for the large errors in the methods now in use. It is then carefully dried and analysed for tannin as in the regular procedure for vegetable-tanned leathers, and from this figure the percentage of tannin in the original material may readily be calculated.

*Presented before the Section of Leather Chemistry of the American Chemical Society, St. Louis, Mo., April 14, 1920.

Sensitivity of Gelatin-Salt Test and its Effect upon the Method.—The gelatin-salt test appears to be the most satisfactory one known for determining whether or not a tan liquor has been completely detannised. In the present official methods, it is assumed that the hide powder completely detannises the liquor because the non-tannin filtrate remains clear upon addition of the gelatin-salt reagent. This reagent, however, gives negative results with extremely dilute solutions of tannin. Another fact tending to make it difficult to detect the presence of small amounts of free tannin in the liquor after shaking with hide powder is that these liquors are always turbid and must be filtered, and it is a known fact that filter paper will remove tannin from solution to some extent. It was therefore essential to determine the sensitivity of the test for the conditions under which the analyses were made.

If the time of shaking, volume of tan liquor, and quantity of hide powder are kept constant, the less the concentration of the liquor the greater will be the fraction of tannin removed by the hide powder. This made it desirable in checking the accuracy of the work to make several sets of analyses for each tanning material examined, using a different concentration of liquor in each case. The most concentrated solution of each material noted in Table I was used to test sensitivity of the gelatin-salt reagent by diluting to greater and greater extent and then filtering and testing with the reagent under the same conditions as employed in the actual analyses. The reagent was added a drop at a time to 10 cc. of the clear filtrate in a test-tube. The dilutions at which the test failed, expressed in cc. of tan liquor diluted to 100 cc., were as follows: quebracho 1, hemlock bark 2, oak bark 2, larch bark 2, chestnut wood 0.5, osage orange 2, sumac 1, and gambier 4. It therefore follows, since the detannised filtrates from all these liquors gave a negative test with the gelatin-salt reagent, that more than 95 per cent of the tannin of the gambier liquor and more than 97 per cent of the tannin of every other liquor were removed from solution by the hide powder. But the analyses were also carried out with much more dilute liquors, from which the hide powder should remove an even greater percentage of the tannin. Since the results obtained for any one material, using several dilutions, checked so closely, we may reasonably conclude that the hide powder removed practically all of the tannin from all solutions which gave no test with the gelatin-salt reagent after the shaking process.

Hide Powder.—The hide powder used in this work is a highly purified product known as American Standard and is prepared by the Standard Mfg. Co. of Ridgway, Pa., especially for use in the analysis of tanning materials. Since this hide powder is of variable composition due to changes in water content, it was necessary to base our calculations upon the protein it contained, to which we shall hereafter refer simply as hide substance. Von Schroeder (Procter, *Loc. cit.*) found hide substance to contain 17.8 per cent of nitrogen, which figure is generally accepted. The per cent of nitrogen determined by the Kjeldahl method, multiplied by 5.62, should therefore give the per cent of hide substance. The hide powder

used in this work showed by analysis:—

	Per cent.
Water	12.29
Ash	0.36
Fat (chloroform extract) ...	0.82
Hide substance (N × 5.62) ...	86.50
Total	99.97

from which it would appear that the factor 5.62 is correct.

Materials Examined.—Eight materials were selected for examination which are fairly extensively used and which show great differences in properties, especially in so-called astringency. The solid quebracho extract and the four liquid extracts of oak bark, larch bark, chestnut wood, and osage orange are typical samples of the best of these materials now on the American market. The gambier is the ordinary pasty product from the East Indies; the sumac, consisting of ground leaves and small twigs, is from a reputable dealer in Palermo; and the hemlock bark came from the forests of Wisconsin.

Procedure.—The extracts were simply dissolved in hot water, cooled slowly, and made up to the mark. The bark and sumac were finely ground and leached by percolation, only the extracted portions being used after making up to definite volume. In each test, 12 grms. of hide powder (of known hide substance content) were put into a wide-mouth, rubber-stoppered, half-pint bottle, the tanning material dissolved in 200 cc. of solution was added, and the whole was shaken in a rotating box for 6 hours.

The amount of material that could be used was limited by the amount of tannin that the hide-powder was capable of taking up in 6 hours. On the other hand it was desirable not to use too little, since the less the amount of tannin fixed per unit of hide substance, the less the accuracy of the method, since the tannin was determined by difference. Whenever the liquor after the 6-hour shaking gave a turbidity or precipitate with the gelatin-salt reagent, the test was repeated with less material. The smallest amount used for any material represents the least we were able to use and still get reproducible results.

The tanned powder was washed by shaking with 200 cc. of water for 30 min., squeezing through a suitable cloth, and repeating the washing operation until the wash-water showed no colour and gave no test with ferric chloride solution. Except for the osage orange and chestnut wood extracts, which are unusual in several respects, not more than 12 washings were required to free the powders from non-tannin, which shows that the line of demarcation between tannin and non-tannin is fairly sharp for the commoner materials. The wash-water continued to extract colouring matter from the powders tanned with osage orange until after the fiftieth washing, while as many as 25 washings were required to free the powders tanned with chestnut wood from soluble matter producing a dark colour with ferric chloride. All wash-water was tested with the gelatin-salt reagent, but in every case the test was negative. This method of washing was found to be more efficient than using running water on a suction filter, probably since of soluble matter from the interior of the hide fibres.

The washed powders were dried at room temperature for 24 hours or longer and then analysed

MATERIAL	Material Grms. per Litre.	Percentage Analysis of Tanned Hide Powder					Per 100 G. of Hide Substance		Tannin in Material Per Cent
		Water	Ash	Fat	Hide Substance (N x 5.62)	Tannin (by Difference)	Tannin Found Grms.	Material Used Grms.	
Quebracho	18.8	11.56	0.14	0.35	74.92	13.03	17.39	36.8	47.26
Quebracho	18.8	11.42	0.08	0.35	75.05	13.10	17.46	36.8	47.45
Quebracho	11.5	13.81	0.03	0.30	77.53	8.33	10.74	22.6	47.52
Hemlock Bark	150.0	9.94	0.12	0.24	76.54	13.16	17.19	287.9	5.97
Hemlock Bark	100.0	10.73	0.13	0.28	79.39	9.47	11.93	191.9	6.22
Hemlock Bark	75.0	12.76	0.05	0.28	79.53	7.38	9.28	147.1	6.31
Oak Bark	67.5	12.54	0.07	0.12	74.76	12.51	16.73	131.6	12.71
Oak Bark	45.0	11.19	0.09	0.24	79.36	9.12	11.49	87.6	13.12
Oak Bark	25.0	13.53	0.05	0.34	81.00	5.08	6.27	48.9	12.82
Larch Bark	67.5	12.59	0.09	0.13	75.61	11.58	15.32	131.6	11.64
Larch Bark	45.0	13.65	0.09	0.30	77.90	8.06	10.35	87.7	11.80
Larch Bark	25.0	16.52	0.08	0.25	78.65	4.50	5.72	48.9	11.70
Chestnut Wood	67.5	12.43	0.11	0.05	75.76	11.65	15.38	131.6	11.60
Chestnut Wood	45.0	12.82	0.13	0.19	78.54	8.32	10.59	87.7	12.08
Chestnut Wood	37.5	12.05	0.10	0.21	80.74	6.90	8.55	71.7	11.92
Sumac	93.8	11.39	0.16	0.36	74.92	13.17	17.58	179.3	9.80
Sumac	62.5	12.26	0.23	0.31	78.38	8.82	11.25	119.5	9.41
Sumac	37.5	11.75	0.12	0.37	81.07	5.79	7.06	73.5	9.61
Osage Orange	48.8	12.82	0.13	0.17	77.35	9.53	12.32	95.0	12.97
Osage Orange	32.5	12.83	0.09	0.25	80.09	6.74	8.42	63.3	13.30
Osage Orange	26.3	12.43	0.12	0.25	81.43	5.77	7.09	51.2	13.85
Gambier	50.0	12.08	0.18	0.19	81.44	6.11	7.50	97.4	7.70
Gambier	49.5	11.77	0.26	0.28	81.70	5.99	7.33	94.7	7.74
Gambier	29.0	13.06	0.14	0.35	82.74	3.71	4.48	56.5	7.93

Table I.

for water, ash, fat, and hide substance. The difference between 100 and the sum of these percentages was taken as the per cent of tannin in the leather. The parts of tannin per 100 parts of hide substance in the leather divided by parts of tanning material used per 100 parts of hide substance gave the fraction of tannin in the original material.

The results for the eight materials examined are given in Table I.

Comparison with A. L. C. A. Method.

Practically all tanning materials are bought and sold in this country on the basis of tannin content as determined by the official method of the American Leather Chemists' Association. The principle of the method is similar to that of the new method as regards the shaking of a solution of the tanning material with hide powder, but differs in that the drop in concentration of the liquor upon shaking is taken as the measure of its tannin content, while the tanned powder is simply discarded. The details of the A. L. C. A. (*J. Amer. Leather Chem. Assoc.*, 1919, xiv., 654) method follow:

The hide powder is specially prepared by giving it a light chrome tannage with chrome alum, washing it practically free from soluble matter, and squeezing it until it contains not less than 71 nor more than 74 per cent of water. The solution of tanning material for analysis must contain not less than 0.375 nor more than 0.425 grms. of tannin per 100 cc., as found by this method. To 200 cc. of this solution is added such an amount of the wet hide powder as contains not

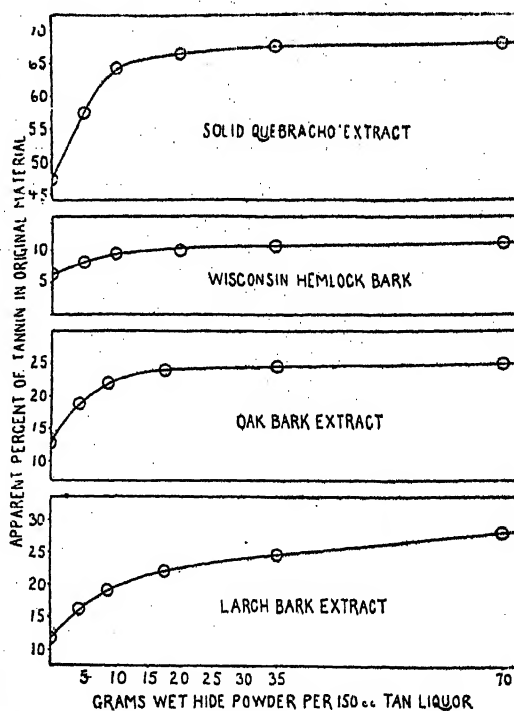


Fig. 1.

less than 12.2 nor more than 12.8 grms. of dry hide powder and the whole is shaken for 10

Percentage Analysis of Material.							
MATERIAL.		Water	A. L. C. A. Method		New Method Tannin	Percentage Error in A. L. C. A. Method	
			Insoluble Matter	Soluble Matter			
				Non-tannin.			Tannin
Quebracho	...	17.87	7.16	6.96	68.01	47.41	43
Hemlock Bark	...	8.90	74.33	6.71	10.06	6.17	63
Oak Bark	...	52.66	3.68	19.46	24.20	12.88	88
Larch Bark	...	51.08	5.88	20.90	22.14	11.71	89
Chestnut Wood	...	58.90	1.50	13.80	25.80	11.90	117
Sumac	...	9.25	47.20	17.99	25.56	9.61	166
Osage Orange	...	46.05	3.45	10.63	39.87	13.37	198
Gambier	...	51.12	5.36	18.57	24.95	7.79	220

Table II.

minutes. The limits defined are to some extent arbitrary, but it has been found necessary to set limits of some sort in order to get concordant results. The detannised solution is separated from the powder by squeezing through linen and is then filtered through paper, after the addition of kaolin, the solution being returned until the filtrate is quite clear. The amount of residue from an aliquot portion of this filtrate, after correcting for the water introduced by the hide powder, is taken as a measure of the non-tannin in the original material. The difference between the total soluble matter and the non-tannin is called tannin.

Several outstanding sources of error in this method were emphasised by the authors in an earlier paper (*J. Amer. Leather Chem. Assoc.*, 1918, xiii., 429). The most serious defect is that it does not take into account the fact that hide powder removes non-tannin of certain kinds, such as gallic acid, pyrocatechol, &c., from solution to an extent depending upon the concentration. These substances do not make leather and are readily washed out. This explains the fact that where tanners try to keep a rigid cost account of tanning materials, they find no such amount of tannin in the leather as would be expected from the amount of tannin used, as determined by the A. L. C. A. method. The analyses of the eight materials by the A. L. C. A. method are given in Table II. along with a calculation of the percentage errors involved in this method, made upon the assumption that the results obtained by the new method are correct.

Although the enormous errors in the A. L. C. A. method are nothing short of sensational, we are convinced that they are not at all exaggerated. The extent of these errors is less surprising, however, when the behaviour of certain non-tannins, like gallic acid, in the presence of hide powder is studied. A series of solutions of gallic acid of different strengths was prepared and treated by the A. L. C. A. method as though they were tan liquors of the required strength. The results for non-tannin should have been 100 per cent in every case if the method were reliable, but the actual data in Table III, show that a very large proportion of the acid is taken up by the hide powder. Table IV. shows that the amount of gallic acid removed from solution is very largely dependent upon the proportion of hide powder employed. Our results by the new method for gambier indicate that this sample contains more than 4 times as much non-tannin as tannin. When we consider that more than 50 per cent of these non-tannins may be removed from solution by the hide powder, errors exceeding 200 per cent are to be expected by the A. L. C. A. method.

Table III.—Results of Treatment of Pure Gallic Acid Solutions by the A. L. C. A. Method.

Using 47 cc. of wet hide powder (73 per cent water) to 200 cc. of solution.

Gallic Acid Gms. per Litre.	Non-tannin Per cent.	Tannin Per cent.
8.88	54.0	46.0
4.44	47.1	52.9
2.22	43.8	56.2
1.11	40.4	59.6

Table IV.—Effect of Altering Proportion of Hide Powder upon Amount of Gallic Acid Removed from a 0.888 per cent Solution.

Using the principle of the A. L. C. A. method.

Wet Hide Powder (73% water) G. per 200 cc.	Non-tannin Per cent	Tannin Per cent
5	91.8	8.2
10	86.0	14.0
25	69.6	30.4
50	52.1	47.9
75	43.7	56.3

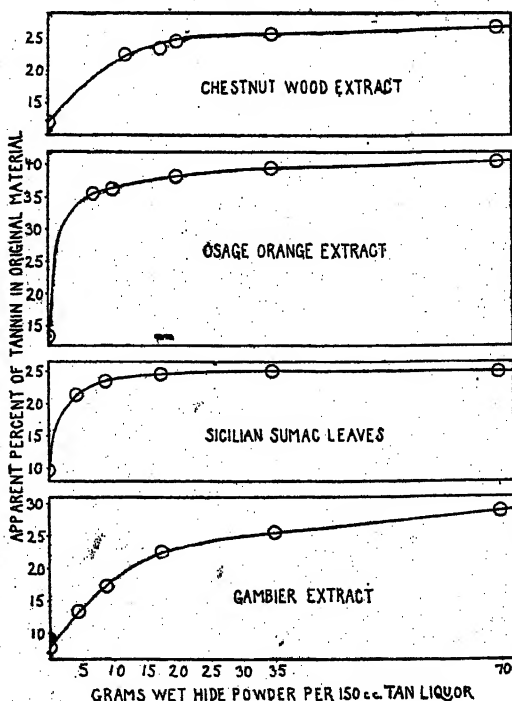


FIG. 1a.

The reason for the necessity of arbitrary limits in the official method is suggested by the gallic acid experiments, but is more strongly emphasised by similar experiments upon actual tan liquors. The effect of altering the proportion of hide powder with solutions of the eight tanning materials is shown in Table V. and Figs. 1 and 1a. The zero points in the figure represent the percentages of tannin found by the new method. In none of these experiments did the solution after shaking give a test with the gelatin-salt reagent, but we nevertheless find enormous increases in per cent of tannin due to increasing the proportion of hide powder. This alone should be sufficient to show that the A. L. C. A. method cannot be considered an exact one and that the arbitrary limits were set so that different analysts would get concordant rather than more nearly correct results. Table V. and Fig. 2 show how the percentage of error increases with increasing proportions of hide powder.

Table V.

MATERIAL.	Grms. per Litre	Wet Hide Powder (73% Water) Used to Detannise 150 cc. Tan Liquor Grms.	Apparent Per cent of Tannin	Percentage Error Due to Hide Powder
Quebracho	3	70.0	68.18	44
		35.0	67.56	43
		20.0	66.61	40
		10.0	64.36	36
		5.0	57.56	21
Hemlock Bark	20	70.0	10.98	78
		35.0	10.60	72
		20.0	9.76	58
		10.0	9.35	52
		5.0	7.98	29
Oak Bark	4.11	70.0	25.02	94
		35.0	24.59	91
		17.5	24.01	86
		8.8	22.09	72
		4.4	18.77	46
Larch Bark	4.37	70.0	28.10	140
		35.0	24.52	109
		17.5	21.97	88
		8.8	19.10	63
		4.4	16.24	39
Chestnut Wood	15	70.0	26.87	126
		35.0	25.80	117
		20.0	24.59	107
		17.5	23.52	98
		12.0	22.49	89
Sumac	4	70.0	24.98	160
		35.0	25.05	161
		17.5	24.47	155
		8.8	23.45	144
		4.4	21.45	123
Osage Orange	8	70.0	40.48	203
		35.0	39.47	195
		20.0	38.21	186
		10.0	36.27	171
		7.0	35.67	167
Gambier	4.58	70.0	29.04	273
		35.0	25.60	229
		17.5	22.56	190
		8.8	17.22	121
		4.4	13.38	72

As might be expected, the greatest errors in the official method are obtained with those materials containing the greatest proportion of non-tannin to tannin. Quebracho having least non-tannin, gives the smallest error. However, if the quebracho is mixed with gallic acid to make the proportion of non-tannin to tannin about the same as in the case of the gambier, it gives errors nearly as great as in the case of the gambier. This is shown in Table VI.

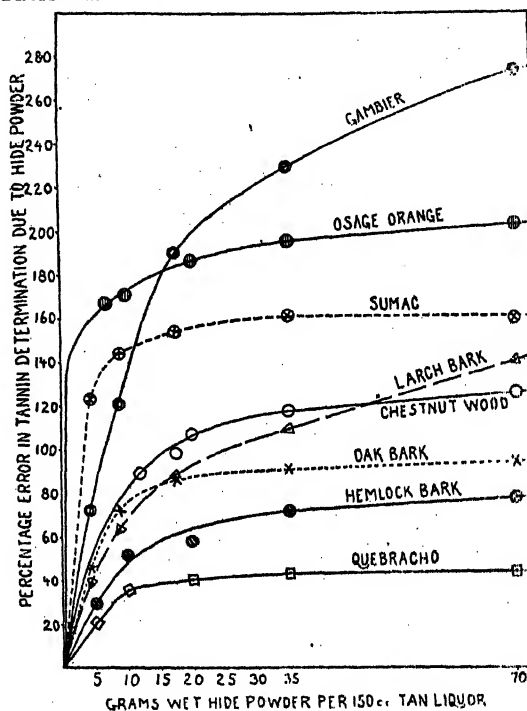


Fig. 2.

Comparison of the two methods has brought out at least one fact of practical significance: Those materials which give the least errors are most astringent, while those giving greatest errors are least astringent. The order of the materials in Table II. might almost be taken as the order of decreasing astringency, although an exact parallelism cannot be claimed since we have no quantitative measure of astringency. Quebracho and hemlock bark are generally conceded to be the most astringent and sumac and gambier the least astringent of these materials. This suggested a relation between astringency and the ratio of non-tannin to tannin. In the experiments listed in Table I., the hide powder fixed more than twice as much tannin from the quebracho liquors in 3 hours as from the gambier liquors in 6 hours. But, when enough gallic acid was added to the stronger quebracho liquors to give them the same proportion of non-tannin to tannin as in the gambier, the hide powder did not remove anywhere nearly all the tannin in 6 hours. Upon addition of the gelatin-salt reagent to the liquors after shaking, huge precipitates were formed, suggesting a great reduction in astringency. That the

Wet Hide Powder (73% Water) Used to Detannise 150 cc. Tan Liquor Grms.	Percentage Analysis of Mixture of 5 Parts of Quebracho Extract to 9 Parts of Dry Gallic Acid					Percentage Error Due to Hide Powder		
	A. L. C. A. Method.					Quebracho		
	Water	Insoluble Matter	Soluble Matter		New Method Tannin	Alone (from Fig. II)	In Presence of Gallic Acid	Gambier (from Table V)
			Non-tannin	Tannin				
4.4	5.80	3.96	63.34	26.90	16.93	18	59	72
8.8	5.80	3.96	53.39	36.85	16.93	33	118	121
17.5	5.80	3.96	44.07	46.17	16.93	39	173	190
35.0	5.80	3.96	37.14	53.10	16.93	43	214	229
70.0	5.80	3.96	33.87	56.37	16.93	44	233	273

Table VI.

effect was only one of slowing up, the tanning action was proved by the fact that the hide powder was able to detannise the solution completely in 24 hours.

Practicability of the New Method.

The new method in its present form requires more time than the A. L. C. A. method, but this disadvantage must be considered negligible compared to the advantage of greatly increased accuracy. If the new method is to prove satisfactory from the standpoint of setting a price on tanning materials, it must give results which are readily reproducible in different laboratories. We are convinced that it will do this quite as well as the official method when the different analysts become used to manipulating it. The several results for any one material in Table I. were determined days, and sometimes weeks, apart. The hide powder used in the new method is not chromed, but is used exactly as it comes from the manufacturer. If, however, it is first chromed, it gives a higher result for osage orange, apparently due to the chrome acting as a mordant for the colouring matter. But this colouring matter does not precipitate gelatin nor does it form a stable compound with unchromed hide fibre and we feel that the method is the more accurate for

not estimating this colouring matter as tannin. The question of putting a value on this colouring matter may have to be solved, but this problem will probably be confined to very few materials. On the whole we believe the new method will be found quite as practicable and certainly very much more satisfactory from the standpoint of accuracy than the present official method. What has been said concerning the A. L. C. A. method applies equally well to the European methods since they differ only in detail.

Summary.

A new method of tannin analysis is described which we believe determines exactly what is called for in the generally accepted definition of tannin from a practical view point, namely, that portion of the water-soluble matter of certain vegetable materials which will precipitate gelatin from solution and which will form compounds with hide fibre which are resistant to washing.

The analyses of eight common tanning materials by the new method and by the official method of the American Leather Chemists' Association indicate that the latter method is in error to the extent of from 43 to 220 per cent.

The new method gives reproducible results and is considered entirely practicable.—*Journal of Industrial and Engineering Chemistry*, May, 1920.

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Academical Year, 1920-21.

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Winter Session commences on Thursday, 14th October, 1920, and closes on Thursday, 17th March, 1921.

Summer Session commences on Tuesday, 19th April, 1921, and closes on Friday, 1st July, 1921.

The Preliminary Examinations will commence on Friday, 10th September, 1920, and Friday, 11th March, 1921.

FACULTY OF SCIENCE.

The Faculty of Science embraces 8 Chairs besides Lecturers by whom instruction is given in all the main departments of the Science School.

PROFESSORS.

Natural Philosophy Charles Niven, M.A., D.Sc., F.R.S.
Physiology John Alex. MacWilliam, M.D., F.R.S.
Anatomy Robert William Reid, M.D., F.R.C.S.
Natural History John Arthur Thomson, M.A., LL.D.
Mathematics Hector Munro Macdonald.

O.B.E., M.A., F.R.S.

Agriculture James Hendrick, B.Sc.
Chemistry Alexander Findlay, M.A., D.Sc., Ph.D.
Botany William Grant Craib, M.A.

LECTURERS.

Veterinary Hygiene William Brown, M.R.C.V.S., F.R.P.S.
Fisheries Thos. A. W. Fulton, M.D.
Geology Alfred Wm. Gibb, M.A., D.Sc.

Engineering Field Work Alex. R. Horne, B.Sc., A.M.I.C.E.

Forestry Peter Leslie, M.A., B.Sc., B.Sc. (Agr.).
Agriculture Wm. J. Profitt, M.A., B.Sc. (Agr.).
Parasitology John Rennie, D.Sc.

Forest Botany and Alex. S. Watt, M.A., B.Sc. (Agr.).
Forest Zoology R. B. Forrester, M.A.
Rural Economics

The Degrees conferred by the University are:—

Bachelor of Science in Pure Science (B.Sc.).

Bachelor of Science in Agriculture (B.Sc. Agr.).

Bachelor of Science in Forestry (B.Sc. For.).

Doctor of Science (D.Sc.).

Diplomas in Agriculture and Forestry are also granted.

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Instruction in special departments of Medical practice is given by Lecturers appointed by the University Court.

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The Degrees in Medicine granted by the University are:—

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Doctor of Medicine (M.D.).

Master of Surgery (Ch.M.).

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UNIVERSITY OF BIRMINGHAM.

FACULTY OF SCIENCE.

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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

CARDIFF, 1920.

INAUGURAL ADDRESS OF THE PRESIDENT.

WILLIAM A. HERDMAN,
C.B.E., D.Sc., Sc.D., LL.D., F.R.S.,
Professor of Oceanography in the University
of Liverpool.

Oceanography and the Sea-Fisheries.

It has been customary, when occasion required, for the President to offer a brief tribute to the memory of distinguished members of the Association lost to Science during the preceding year. These, for the most part, have been men of advanced years and high reputation, who had completed their life-work and served well in their day the Association and the sciences which it represents. We have this year no such losses to record. But it seems fitting on the present occasion to pause for a moment and devote a grateful thought to that glorious band of fine young men of high promise in science who, in the years since our Australian meeting in 1914, gave, it may be, in brief days and months of sacrifice, greater service to humanity and the advance of civilisation than would have been possible in years of normal time and work. A few names stand out already known and highly honoured—Mosely, Jenkinson, Geoffrey Smith, Keith Lucas, Gregory, and more recently Leonard Doncaster—all grievous losses; but there are also others, younger members of our Association, who had not yet had opportunity for showing accomplished work, but who equally gave up all for a great ideal. I prefer to offer a collective rather than an individual tribute. Other young men of science will arise and carry on their work—but the gap in our ranks remains. Let their successors remember that it serves as a reminder of a great example and of high endeavour worthy of our gratitude and of permanent record in the annals of Science.

At the last Cardiff Meeting of the British Association in 1891 you had as your President the eminent astronomer Sir William Huggins, who discoursed upon the then recent discoveries of the spectroscope in relation to the chemical nature, density, temperature, pressure and even the motions of the stars. From the sky to the sea is a long drop; but the sciences of both have this in common that they deal with fundamental principles and with vast numbers. Over three hundred years ago Spenser in the "Faerie Queene" compared "the seas abundant progeny" with "the starres on hy," and recent investigations show that a litre of sea-water may contain more than a hundred times as many living organisms as there are stars visible to the eye on a clear night.

During the past quarter of a century great advances have been made in the science of the sea, and the aspects and prospects of sea-fisheries research have undergone changes which encourage the hope that a combination of the work now carried on by hydrographers and biologists in most civilised countries on fundamental problems of the ocean may result in a more rational exploitation and administration of the fishing industries.

And yet even at your former Cardiff Meeting thirty years ago there were at least three papers of oceanographic interest—one by Professor Osborne Reynolds on the action of waves and currents, another by Dr. H. R. Mill on seasonal variation in the temperature of lochs and estuaries, and the third by our Honorary Local Secretary for the present meeting, Dr. Evans Hoyle, on a deep-sea tow-net capable of being opened and closed under water by the electric current.

It was a notable meeting in several other respects, of which I shall merely mention two. In Section A, Sir Oliver Lodge gave the historic address in which he expounded the urgent need, in the interests of both science and the industries, of a national institution for the promotion of physical research on a large scale. Lodge's pregnant idea put forward at this Cardiff Meeting, supported and still further elaborated by Sir Douglas Galton as President of the Association at Ipswich, has since borne notable fruit in the establishment and rapid development of the National Physical Laboratory. The other outstanding event of that meeting is that you then appointed a committee of eminent geologists and naturalists to consider a project for boring through a coral reef, and that led during following years to the successive expeditions to the atoll of Funafuti in the Central Pacific, the results of which, reported upon eventually by the Royal Society, were of great interest alike to geologists, biologists, and oceanographers.

Dr. Huggins, on taking the Chair in 1891, remarked that it was over thirty years since the Association had honoured Astronomy in the selection of its President. It might be said that the case of Oceanography is harder, as the Association has never had an Oceanographer as President—and the Association might well reply "Because until very recent years there has been no Oceanographer to have." If Astronomy is the oldest of the sciences, Oceanography is probably the youngest. Depending as it does upon the methods and results of other sciences, it was not until our knowledge of Physics, Chemistry, and Biology were relatively far advanced that it became possible to apply that knowledge to the investigation and explanation of the phenomena of the ocean. No one man has done more to apply such knowledge derived from various other subjects and to organise the results as a definite branch of science than the late Sir John Murray, who may therefore be regarded as the founder of modern Oceanography.

It is, to me, a matter of regret that Sir John Murray was never President of the British Association. I am revealing no secret when I tell you that he might have been. On more than one occasion he was invited by the Council to accept nomination and he declined for reasons that were good and commanded our respect. He felt that

the necessary duties of this post would interfere with what he regarded as his primary life-work—oceanographical explorations already planned, and the last of which he actually carried out in the North Atlantic in 1912, when over seventy years of age, in the Norwegian steamer *Michael Sars* along with his friend Dr. Johan Hjort.

Anyone considering the subject-matter of this new science must be struck by its wide range overlapping as it does the borderlands of several other sciences and making use of their methods and facts in the solution of its problems. It is not only world-wide in its scope but extends beyond our globe and includes astronomical data in their relation to tidal and certain other oceanographical phenomena. No man in his work or even thought, can attempt to cover the whole ground—although Sir John Murray, in his remarkably comprehensive "Summary" volumes of the *Challenger* Expedition and other writings, went far towards doing so. He, in his combination of physicist, chemist, geologist, and biologist, was the nearest approach we have had to an all-round Oceanographer. The International Research Council probably acted wisely at the recent Brussels Conference in recommending the institution of two International Sections in our subject, the one of physical and the other of biological Oceanography—although the two overlap and are so interdependent that no investigator on the one side can afford to neglect the other.*

On the present occasion I must restrict myself almost wholly to the latter division of the subject, and be content, after brief reference to the founders and pioneers of our science, to outline a few of those investigations and problems which have appeared to me to be of fundamental importance, of economic value, or of general interest.

Although the name Oceanography was only given to this branch of science by Sir John Murray in 1880, and although according to that veteran oceanographer Mr. J. Y. Buchanan, the last surviving member of the civilian staff of the *Challenger*, the science of Oceanography was born at sea on February 5, 1873,† when, at the first official dredging station of the expedition, to the westward of Tenerife, at 1525 fathoms, everything that came up in the dredge was new and led to fundamental discoveries as to the deposits forming on the floor of the ocean, still it may be claimed that the foundations of the science were laid by various explorers of the ocean at much earlier dates. Aristotle, who took all knowledge for his province, was an early oceanographer on the shores of Asia Minor. When Pytheas passed between the pillars of Hercules into the unknown

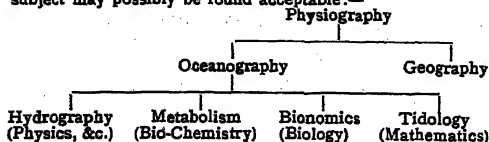
Atlantic and penetrated to British seas in the fourth century B.C., and brought back reports of Ultima Thule and of a sea to the North thick and sluggish like a jelly-fish, he may have been recording an early planktonic observation. But passing over all such and many other early records of phenomena of the sea, we come to surer ground in claiming, as founders of Oceanography, Count Marsili, an early investigator of the Mediterranean, and that truly scientific navigator Captain James Cook, who sailed to the South Pacific on a Transit of Venus expedition in 1769 with Sir Joseph Banks as naturalist, and by subsequently circumnavigating the South Sea about latitude 60° finally disproved the existence of a great southern continent; and Sir James Clerk Ross, who, with Sir Joseph Hooker as naturalist, first dredged the Antarctic in 1840.

The use of the naturalist's dredge (introduced by O. F. Müller, the Dane, in 1799) for exploring the sea-bottom was brought into prominence almost simultaneously in several countries of North-West Europe—by Henri Milne-Edwards in France in 1830, Michael Sars in Norway in 1835, and our own Edward Forbes about 1832.

The last-mentioned genial and many-sided genius was a notable figure in several sections of the British Association from about 1836 onwards, and may fairly be claimed as a pioneer of Oceanography. In 1839 he and his friend the anatomist, John Goodsir, were dredging in the Shetland seas, with results which Forbes made known to the meeting of the British Association at Birmingham that summer, with such good effect that a "Dredging Committee"‡ of the Association was formed to continue the good work. Valuable reports on the discoveries of that Committee appear in our volumes at intervals during the subsequent twenty-five years.

It has happened over and over again in history that the British Association, by means of one of its research committees, has led the way in some important new research or development of science and has shown the Government or an industry what wants doing and how it can be done. We may fairly claim that the British Association has inspired and fostered that exploration of British seas which through marine biological investigations and deep-sea expeditions has led on to modern Oceanography. Edward Forbes and the British Association Dredging Committee, Wyville Thomson, Carpenter, Gwyn Jeffreys, Norman, and other naturalists of the pre-*Challenger* days—all these men in the quarter-century from 1840 onwards worked under research committees of the British Association, bringing their results before successive meetings; and some of our older volumes enshrine classic reports on dredging by Forbes, McAndrew, Norman, Brady, Alder, and other notable naturalists of that day. These local researches paved the way for the *Challenger* and other national deep-sea expeditions. Here as in other cases, it required private enterprise to precede and stimulate Government action.

* The following classification of the primary divisions of the subject may possibly be found acceptable:—



† Others might put the date later. Significant publications are Sir John Murray's Summary Volumes of the *Challenger* (1895), the inauguration of the "Musée Océanographique" at Monaco in 1910, the foundation of the "Institut Océanographique" at Paris in 1906 (see the Prince of Monaco's letter to the Minister of Public Instruction), and Sir John Murray's little book "The Ocean" (1913), where the superiority of the term Oceanography to Thalassography (used by Alexander Agassiz) is discussed.

‡ "For researches with the dredge, with a view to the investigation of the marine zoology of Great Britain, the illustration of the geographical distribution of marine animals, and the more accurate determination of the fossils of the pleistocene period: under the superintendence of Mr. Gray, Mr. Forbes, Mr. Goodsir, Mr. Patterson, Mr. Thomson of Belfast, Mr. Ball of Dublin, Dr. George Johnston, Mr. Smith of Jordan Hill, and Mr. A. Strickland, &c. Report for 1839, p. 26.

It is probable that Forbes and his fellow-workers on this "Dredging Committee" in their marine explorations did not fully realise that they were opening up a most comprehensive and important department of knowledge. But it is also true that in all his expeditions—in the British seas from the Channel Islands to the Shetlands, in Norway, in the Mediterranean as far as the Ægean Sea—his broad outlook on the problems of nature was that of the modern oceanographer, and he was the spiritual ancestor of men like Sir Wyville Thomson of the *Challenger* Expedition and Sir John Murray, whose accidental death a few years ago, while still in the midst of active work, was a grievous loss to this new and rapidly advancing science of the sea.

Forbes in these marine investigations worked at border-line problems, dealing for example with the relations of Geology to Zoology, and the effect of the past history of the land and sea upon the distribution of plants and animals at the present day, and in these respects he was an early oceanographer. For the essence of that new subject is that it also investigates border-line problems and is based upon and makes use of all the older fundamental sciences—Physics, Chemistry, and Biology—and shows for example how variations in the great ocean currents may account for the movements and abundance of the migratory fishes, and how periodic changes in the physico-chemical characters of the sea, such as variations in the hydrogen-ion and hydroxyl-ion concentration, are correlated with the distribution at the different seasons of the all-important microscopic organisms that render our oceanic waters as prolific a source of food as the pastures of the land.

Another pioneer of the nineteenth century who I sometimes think, has not yet received sufficient credit for his foresight and initiative, is Sir Wyville Thomson, whose name ought to go down through the ages as the leader of the scientific staff on the famous *Challenger* Deep-Sea Exploring Expedition. It is due chiefly to him and to his friend Dr. W. B. Carpenter that the British Government, through the influence of the Royal Society, was induced to place at the disposal of a committee of scientific experts first the small surveying steamer *Lightning* in 1868, and then the more efficient steamer *Porcupine* in the two succeeding years, for the purpose of exploring the deep water of the Atlantic from the Faroes in the North to Gibraltar and beyond in the South, in the course of which expeditions they got successful hauls from the then unprecedented depth of 2435 fathoms, nearly three statute miles.

It will be remembered that Edward Forbes, from his observations in the Mediterranean (an abnormal sea in some respects), regarded depths of over 300 fathoms as an azoic zone. It was the work of Wyville Thomson and his colleagues Carpenter and Gwyn Jeffreys on these successive dredging expeditions to prove conclusively what was beginning to be suspected by naturalists, that there is no azoic zone in the sea, but that abundant life belonging to many groups of animals extends down to the greatest depths of from four to five thousand fathoms—nearly six statute miles from the surface.

These pioneering expeditions in the *Lightning* and *Porcupine*—the results of which are not even yet fully made known to science—were epoch-

making, inasmuch as they not only opened up this new region to the systematic marine biologist, but gave glimpses of world-wide problems in connection with the physics, the chemistry, and the biology of the sea which are only now being adequately investigated by the modern oceanographer. These results, which aroused intense interest amongst the leading scientific men of the time, were so rapidly surpassed and overshadowed by the still greater achievements of the *Challenger* and other national exploring expeditions that followed in the 'seventies and 'eighties of last century, that there is some danger of their real importance being lost sight of; but it ought never to be forgotten that they first demonstrated the abundance of life of a varied nature in depths formerly supposed to be azoic, and, moreover, that some of the new deep-sea animals obtained were related to extinct forms belonging to the Jurassic, Cretaceous, and Tertiary periods.

It is interesting to recall that our Association played its part in promoting the movement that led to the *Challenger* Expedition. Our General Committee at the Edinburgh Meeting of 1871 recommended that the President and Council be authorised to co-operate with the Royal Society in promoting "a Circumnavigation Expedition, specially fitted out to carry the Physical and Biological Exploration of the Deep Sea into all the Great Oceanic Areas"; and our Council subsequently appointed a committee consisting of Dr. Carpenter, Professor Huxley, and others to co-operate with the Royal Society in carrying out these objects.

It has been said that the *Challenger* Expedition will rank in history with the voyages of Vasco da Gama, Columbus, Magellan, and Cook. Like these it added new regions of the globe to our knowledge, and the wide expanses thus opened up for the first time the floors of the oceans, though less accessible, are vaster than the discoveries of any previous exploration.

Sir Wyville Thomson, although leader of the expedition, did not live to see the completed results, and Sir John Murray will be remembered in the history of science as the *Challenger* naturalist who brought to a successful issue the investigation of the enormous collections and the publication of the scientific results of that memorable voyage: these two Scots share the honour of having guided the destinies of what is still the greatest oceanographic exploration of all times.

In addition to taking his part in the general work of the expedition, Murray devoted special attention to three subjects of primary importance in the science of the sea, viz.: (1) the plankton or floating life of the oceans; (2) the deposits forming on the sea bottoms; and (3) the origin and mode of formation of coral reefs and islands. It was characteristic of his broad and synthetic outlook on nature that, in place of working at the speciology and anatomy of some group of organisms, however novel, interesting, and attractive to the naturalist the deep-sea organisms might seem to be, he took up wide-reaching general problems with economic and geological as well as biological applications.

Each of the three main lines of investigation—deposits, plankton, and coral reefs—which Murray undertook on board the *Challenger* has been most fruitful of results both in his own hands and those

of others. His plankton work has led on to those modern planktonic researches which are closely bound up with the scientific investigation of our sea-fisheries.

His work on the deposits accumulating on the floors of the ocean resulted, after years of study in the laboratory as well as in the field in collaboration with the Abbé Renard of the Brussels Museum, afterwards Professor at Ghent, in the production of the monumental "Deep-Sea Deposits" volume, one of the *Challenger* Reports, which first revealed to the scientific world the detailed nature and distribution of the varied submarine deposits of the globe and their relation to the rocks forming the crust of the earth.

These studies led, moreover, to one of the romances of science which deeply influenced Murray's future life and work. In accumulating material from all parts of the world and all deep-sea exploring expeditions for comparison with the *Challenger* series, some ten years later, Murray found that a sample of rock from Christmas Island in the Indian Ocean, which had been sent to him by Commander (now Admiral) Aldrich, of H.M.S. *Egeria*, was composed of a valuable phosphatic material. This discovery in Murray's hands gave rise to a profitable commercial undertaking, and he was able to show that some years ago the British Treasury had already received in royalties and taxes from the island considerably more than the total cost of the *Challenger* Expedition.

That first British circumnavigating expedition on the *Challenger* was followed by other national expeditions (the American *Tuscarora* and *Albatross*, the French *Travailleur*, the German *Gauss*, *National*, and *Valdivia*, the Italian *Vettor Pisani*, the Dutch *Siboga*, the Danish *Thor* and others) and by almost equally celebrated and important work by unofficial oceanographers such as Alexander Agassiz, Sir John Murray with Dr. Hjort in the *Michael Sars*, and the Prince of Monaco in his magnificent ocean-going yacht, and by much other good work by many investigators in smaller and humbler vessels. One of these supplementary expeditions I must refer to briefly because of its connection with sea-fisheries. The *Triton*, under Tizard and Murray, in 1882, while exploring the cold and warm areas of the Faroe Channel separated by the Wyville-Thomson ridge, incidentally discovered the famous Dubh-Artach fishing-grounds, which have been worked by British trawlers ever since.

Notwithstanding all this activity during the last forty years since Oceanography became a science, much has still to be investigated in all seas in all branches of the subject. On pursuing any line of investigation one very soon comes up against a wall of the unknown or a maze of controversy. Peculiar difficulties surround the subject. The matters investigated are often remote and almost inaccessible. Unknown factors may enter into every problem. The samples required may be at the other end of a rope or a wire eight or ten miles long, and the oceanographer may have to grope for them literally in the dark and under other difficult conditions which make it uncertain whether his samples when obtained are adequate and representative, and whether they have undergone any change since leaving their natural environment. It is not surprising then that in the

progress of knowledge mistakes have been made and corrected, that views have been held on what seemed good scientific grounds which later on were proved to be erroneous. For example, Edward Forbes, in his division of life in the sea into zones on what then seemed to be sufficiently good observations in the Ægean, but which we now know to be exceptional, placed the limit of life at 300 fathoms, while Wyville Thomson and his fellow-workers on the *Porcupine* and the *Challenger* showed that there is no azoic zone even in the great abysses.

Or, again, take the celebrated myth of "Bathybius." In the 'sixties of last century samples of Atlantic mud, taken when surveying the bottom for the first telegraph cables and preserved in alcohol, were found when examined by Huxley, Hæckel, and others to contain what seemed to be an exceedingly primitive protoplasmic organism, which was supposed on good evidence to be widely extended over the floor of the ocean. The discovery of this Bathybius was said to solve the problem of how the deep-sea animals were nourished in the absence of seaweeds. Here was a widespread protoplasmic meadow upon which other organisms could graze. Belief in Bathybius seemed to be confirmed and established by Wyville Thomson's results in the *Porcupine* Expedition of 1869, but was exploded by the naturalists on the *Challenger* some five years later. Buchanan in his recently published "Accounts Rendered" tells us how he and his colleague Murray were keenly on the look-out for hours at a time on all possible occasions for traces of this organism, and how they finally proved, in the spring of 1875 on the voyage between Hong Kong and Yokohama, that the all-pervading substance like coagulated mucus was an amorphous precipitate of sulphate of lime thrown down from the sea-water in the mud on the addition of a certain proportion of alcohol. He wrote to this effect from Japan to Professor Crum Brown, and it is in evidence that after receiving this letter Crum Brown interested his friends in Edinburgh by showing them how to make Bathybius in the chemical laboratory. Huxley at the Sheffield Meeting of the British Association in 1879 handsomely admitted that he had been mistaken, and it is said that he characterised Bathybius as "not having fulfilled the promise of its youth." Will any of our present oceanograph beliefs share the fate of Bathybius in the future? Some may, but even if they do they may well have been useful steps in the progress of science. Although like Bathybius they may not have fulfilled the promise of their youth, yet, we may add, they will not have lived in the minds of man in vain.

Many of the phenomena we encounter in oceanographic investigations are so complex, are or may be affected by so many diverse factors, that it is difficult, if indeed possible, to be sure that we are unravelling them aright and that we see the real causes of what we observe.

Some few things we know approximately—nothing completely. We know that the greatest depths of the ocean, about six miles, are a little greater than the highest mountains on land, and Sir John Murray has calculated that if all the land were washed down into the sea the whole globe would be covered by an ocean averaging

about two miles in depth.* We know the distribution of temperatures and salinities over a great part of the surface and a good deal of the bottom of the oceans, and some of the more important oceanic currents have been charted and their periodic variations, such as those of the Gulf Stream, are being studied. We know a good deal about the organisms floating or swimming in the surface waters (the epi-plankton), and also those brought up by our dredges and trawls from the bottom in many parts of the world—although every expedition still makes large additions to knowledge. The region that is least known to us, both in its physical conditions and also its inhabitants, is the vast done of intermediate waters lying between the upper few hundred fathoms and the bottom. That is the region that Alexander Agassiz from his observations with closing tow-nets on the *Blake* Expedition supposed to be destitute of life, or at least, as modified by his later observations on the *Albatross*, to be relatively destitute compared with the surface and the bottom, in opposition to the contention of Murray and other oceanographers that an abundant meso-plankton was present, and that certain groups of animals, such as the Challengerida and some kinds of Medusæ, were characteristic of these deeper zones. I believe that, as sometimes happens in scientific controversies, both sides were right up to a point, and both could support their views upon observations from particular regions of the ocean under certain circumstances.

But much still remains unknown or only imperfectly known even in matters that have long been studied and where practical applications of great value are obtained—such as the investigation and prediction of tidal phenomena. We are now told that theories require re-investigation and that published tables are not sufficiently accurate. To take another practical application of oceanographic work, the ultimate causes of variations in the abundance, in the sizes, in the movements, and in the qualities of the fishes of our coastal industries are still to seek, and notwithstanding volumes of investigation and a still greater volume of discussion, no man who knows anything of the matter is satisfied with our present knowledge of even the best-known and economically most important of our fishes such as the Herring, the Cod, the Plaice, and the Salmon.

Take the case of our common fresh-water eel as an example of how little we know and at the same time of how much has been discovered. All the eels of our streams and lakes of N.-W. Europe live and feed and grow under our eyes without reproducing their kind—no spawning eel has ever been seen. After living for years in immaturity, at last near the end of their lives the large male and female yellow eels undergo a change in appearance and in nature. They acquire a silvery colour and their eyes enlarge, and in this bridal attire they commence the long journey which ends in maturity, reproduction, and death. From all the fresh waters they migrate in the autumn to the coast, from the inshore seas to the open ocean and still westward and south to the mid-Atlantic and we know not how much further—for the exact

locality and manner of spawning has still to be discovered. The youngest known stages of the *Leptocephalus*, the larval stage of eels, have been found by the Dane, Dr. Johannes Schmidt, to the west of the Azores where the water is over 1000 fathoms in depth. These were about one-third of an inch in length and were probably not long hatched. I cannot now refer to all the able investigators—Grassi, Hjort, and others—who have discovered and traced the stages of growth of the *Leptocephalus* and its metamorphosis into the “elvers” or young eels which are carried by the North Atlantic drift back to the coasts of Europe and ascend our rivers in spring in countless myriads; but no man has been more indefatigable and successful in the quest than Dr. Schmidt, who in the various expeditions of the Danish Investigation Steamer *Thor* from 1904 onwards found successively younger and younger stages, and who is during the present summer engaged in a traverse of the Atlantic to the West Indies in the hope of finding the missing link in the chain, the actual spawning fresh-water eel in the intermediate waters somewhere above the abysses of the open ocean.†

Again, take the case of an interesting oceanographic observation which, if established, may be found to explain the variations in time and amount of important fisheries. Otto Pettersson in 1910 discovered by his observations in the Gullmar Fjord the presence of periodic submarine waves of deeper saltier water in the Kattegat and the fjords of the west coast of Sweden, which draw in with them from the Jutland banks vast shoals of the herrings which congregate there in autumn. The deeper layer consists of “bank-water” of salinity 32 to 34 per thousand, and as this rolls in along the bottom as a series of huge undulations it forces out the overlying fresher water, and so the herrings living in the bankwater outside are sucked into the Kattegat and neighbouring fjords and give rise to important local fisheries. Pettersson connects the crests of the submarine waves with the phases of the moon. Two great waves of saltier water which reached up to the surface took place in November, 1910, one near the time of full moon and the other about new moon, and the latter was at the time when the shoals of herring appeared inshore and provided a profitable fishery. The coincidence of the oceanic phenomena with the lunar phases is not, however, very exact and doubts have been expressed as to the connection; but if established, and even if found to be due not to the moon but to prevalent winds or the influence of ocean currents, this would be a case of the migration of fishes depending upon mechanical causes, while in other cases it is known that migrations are due to spawning needs or for the purpose of feeding, as in the case of the cod and the herring in the west and north of Norway and in the Barents Sea.

Then, turning to a very fundamental matter of purely scientific investigation, we do not know with any certainty what causes the great and all-important seasonal variations in the plankton (or floating minute life of the sea) as seen, for example, in our own home seas, where there is a

* It was possibly in such a former world-wide ocean of ionised water that according to the recent speculations of A. H. Church (Thalassiophyta, 1919) the first living organisms were evoked to become later the floating unicellular plants of the primitive plankton.

† According to Schmidt's results the European fresh-water eel, in order to be able to propagate, requires a depth of at least 500 fathoms, a salinity of more than 35.90 per mille and a temperature of more than 70° C. in the required depth.

sudden awakening of microscopic plant life, the Diatoms, in early spring when the water is at its coldest. In the course of a few days the upper layers of the sea may become so filled with organisms that a small silk net towed for a few minutes may capture hundreds of millions of individuals. And these myriads of microscopic forms, after persisting for a few weeks, may disappear as suddenly as they came to be followed by swarms of Copepoda and many other kinds of minute animals, and these again may give place in the autumn to a second maximum of Diatoms or of the closely related Peridinales. Of course, there are theories as to all these more or less periodic changes in the plankton, such as Liebig's "law of the minimum," which limits the production of an organism by the amount of that necessity of existence which is present in least quantity, it may be nitrogen or silicon or phosphorus. According to Raben it is the accumulation of silicic acid in the sea-water that determines the great increase of Diatoms in spring and again in autumn. Some writers have considered these variations in the plankton to be caused largely by changes in temperature supplemented, according to Ostwald, by the resulting changes in the viscosity of the water; but Murray and others are more probably correct in attributing the spring development of phyto-plankton to the increasing power of the sunlight and its value in photosynthesis.

Let us take the next fact—if it be a fact—that the genial warm waters of the tropics support a less abundant plankton than the cold polar seas. The statement has been made and supported by some investigators and disputed by others, both on a certain amount of evidence. This is possibly a case like some other scientific controversies where both sides are partly in the right, or right under certain conditions. At any rate there are marked exceptions to the generalisation. The German Plankton Expedition in 1889 showed in its results that much larger hauls of plankton per unit volume of water were obtained in the temperate North and South Atlantic than in the tropics between, and that the warm Sargasso Sea had a remarkably scanty microflora. Other investigators have since reported more or less similar results. Lohmann found the Mediterranean plankton to be less abundant than that of the Baltic, gatherings brought back from tropical seas are frequently very scanty, and enormous hauls on the other hand have been recorded from Arctic and Antarctic seas. There is no doubt about the large gatherings obtained in northern waters. I have myself in a few minutes' haul of a small horizontal net in the North of Norway collected a mass of the large Copepod *Calanus finmarchicus* sufficient to be cooked and eaten like potted shrimps by half a dozen of the yacht's company, and I have obtained similar large hauls in the cold Labrador current near Newfoundland. On the other hand, Kofoid and Alexander Agassiz have recorded large hauls of plankton in the Humboldt current off the west coast of America, and during the *Challenger* Expedition some of the largest quantities of plankton were found in the equatorial Pacific. Moreover it is common knowledge that on occasions vast swarms of some planktonic organism may be seen in tropical waters. The yellow alga *Trichodesmium*, which

is said to have given its name to the Red Sea and has been familiarly known as "sea-sawdust" since the days of Cook's first voyage, may cover the entire surface over considerable areas of the Indian and South Atlantic Oceans; and some pelagic animals such as Salpæ, Medusæ, and Ctenophores are also commonly present in abundance in the tropics (see Journal of Sir Joseph Banks; This and other swarms were also noticed by Darwin during the voyage of the *Beagle*). Then, again, American biologists have pointed out that the warm waters of the West Indies and Florida may be noted for the richness of their floating life for periods of years, while at other times the pelagic organisms become rare and the region is almost a desert sea (A. Agassiz, A. G. Mayer, and H. B. Bigelow).

It is probable, on the whole, that the distribution and variations of oceanic currents have more than latitude or temperature alone to do with any observed scantiness of tropical plankton. These mighty rivers of the ocean in places teem with animal and plant life, and may sweep abundance of food from one region to another in the open sea.

(To be continued).

ISOTOPISM.

By J. FREDERICK CORRIGAN.

(Concluded from p. 90.)

Isotopes of Other Elements.—F. W. Ashton in 1913 ("Homogeneity of Atmospheric Neon," British Association, Birmingham Meeting, 1913) stated that he had obtained evidence of a second form of the element neon of atomic weight 22, the atomic weight of ordinary neon being 20. These two isotopes had identical spectra and chemical properties, and only differed from each other in density. An attempt was immediately made to separate the two isotopes, and the gas was fractionated over charcoal cooled in liquid air. No separation, however, of the constituents was effected. A series of fractional diffusions of the gas resulted in a partial separation of the constituents as was evidenced by a change in the density of the two fractions. Quite recently, however, Ashton has effected a separation of the two isotopes, and has identified their presence by the use of Sir J. J. Thomson's positive-ray analysis. By this method he has also obtained indications of a third isotope of mass 21.

Ashton has also very recently submitted other elements to positive-ray analysis (*Nature*, Dec. 18, 1919; March 4, 1920; July 1, 1920). By means of observations of the "mass-spectra" of these elements, he has obtained conclusive evidence of their mixed nature. Chlorine, he has shown to consist of at least two isotopes of atomic weight 35 and 37 respectively. Argon is also considered to consist of two components, and mercury to contain five. Krypton has been shown to be composed of six isotopes of mass 78, 80, 82, 83, 84, and 86. Oxygen, nitrogen, and carbon, however, are considered to be "pure" elements. Fluorine is also a simple element, but bromine is interesting on account of it having an atomic weight of nearly 80, but being composed of equal parts of isotopes of mass 79 and 81. The element boron is complex, having two isotopes of mass

10 and 11. The results obtained from silicon are rather doubtful. They lead to the conclusion that it has two isotopes of mass 28 and 29 respectively, and possibly one of 30. Phosphorus, arsenic, and sulphur are apparently simple elements, although in the latter element, traces of isotopes may exist.

Harkins (*Nature*, April 22, 1920) considers that among the lighter elements, magnesium and silicon are also mixtures of isotopes. He also states that nickel, copper, zinc, and nearly all the other elements between atomic numbers 28 and 30 are mixtures of isotopes.

He has attempted to separate chlorine into its constituent isotopes by diffusion of HCl gas, and he has obtained isotopes of mass 25 and 27 respectively, thus confirming Ashton's results.

The atomic weight of ordinary hydrogen is 1.0077. This he considers to be due to the existence of a meta-hydrogen of mass 3.

Soddy (*Phil. Mag.*, 1920, xxxix., 233), on the other hand, suggests that although the lines obtained in the mass-spectra of hydrogen indicate that the mass of the element is greater than unity, and in agreement with the chemical value of 1.008, yet no isotope has been detected, and thus hydrogen may be regarded as an element free from isotopes.

At this stage, it is interesting to note that Nicholson's work on the constitution of the elements has brought into question the probability of the existence of elements, which although unknown in terrestrial regions, may possibly be present in other portions of the universe (*Phil. Mag.*, 1914, xxvii., 541; xxviii., 630). One of them—*Coronium*—is present in the sun; another—*Nebulium*—has been detected in certain nebulae, whilst the third—*Proto-fluorine*—is as yet unknown.

It has been pointed out, however, that there are no places for these elements in the periodic table, unless they are regarded as isotopes of hydrogen. It would follow, therefore, that the evidence for and against the existence of isotopes of hydrogen is not conclusive, and until further work has been performed on the matter, the isotopes of hydrogen, if any, will remain purely hypothetical.

The Separation of Isotopes.—The proof of the existence of isotopes is one thing, but their separation is indeed quite a different matter. The "elements" of the periodic table may be looked upon as representing the ultimate end to which chemical methods of analysis may be taken. They are types of elements more than actual homogeneous elements themselves. As an analogy, we may walk along a main thoroughfare, and mentally separate all the different architectural styles of the buildings which we meet. But even then, when we have classified all the available structures in accordance with their different designs, on closer examination one should find that, although two or more houses were built on exactly the same lines as one another, they would show minor differences when examined in detail. In precisely the same manner, the periodic table may be considered to represent the different groupings or "styles" of the elements, and as in the analogy of the main thoroughfare, on closer examination we are beginning to find that elements, although possessing the same "style" may differ in detail from each other.

The question of the separation of the isotopic elements has thus come to be one of the leading problems of the day in chemical science. In practice, however, the methods which can be chosen to attain this end are very few indeed. Numerous suggestions have been put forward, suggestions which in theory may possibly be correct, but which have usually led to more or less unsatisfactory results.

Since, however, the isotopic elements exhibit identical chemical characteristics, and only differ from each other in atomic weight, the only plausible methods by which their separation can be effected are those which are able to utilise their properties of mass or weight.

The use of Sir J. J. Thomson's method of positive-ray analysis has proved invaluable in detecting the presence of isotopes in ordinary elements. (For a detailed account of this method, vide *Proc. Roy. Soc.*, 1913, 894). Essentially, this method involves the deflection of the trajectories of ions by the influence of magnetic and electric fields. By the applications of these forces two deflections are produced, each at right angles to the direction in which the ion is moving. A photographic plate is placed at right angles to the path of the ions, and all the particles possessing identical ratios of the charge to the mass fall on the plate on a parabola. The number of variable ions present may then be found from the number of parabolas formed.

The theoretical aspects underlying the possibility of the separation of isotopes have been investigated by Lindemann and Ashton (*Phil. Mag.*, May, 1919). They treated the subject thermodynamically, and in an extensive paper they came to the conclusion that, theoretically, isotopes must be separable, even chemically, under certain conditions. The separation effected, however, would be small, and the requisite conditions could only be obtained with great difficulty.

They also considered physical methods of separation, but the conclusion was arrived at that even by these methods an easy separation of isotopic elements would not be practicable. When the quantities of isotopes dealt with were fairly large, the separation would be small, and when anything approaching complete separation could be hoped for, the yield would be microscopically small. These conclusions were fully borne out by experimental work.

It has been suggested that if an "elementary" isotopic gas or liquid be centrifuged, a partial separation of the isotopes could be effected, and that the concentration of the heavier constituent at the edge of the mass of substance would be greater than in the centre. Applying this principle to actual experiment, it was found to give tolerably good results, and indeed, according to Ashton (*Phil. Mag.*, May, 1919), the use of the centrifuge would appear to constitute one of the most promising methods of effecting the separation of isotopic bodies, provided that the considerably difficult engineering problems involved in the process could be overcome.

General Considerations. The Influence of Isotopism on the Theories of Atomic Evolution. The "Whole-Number Rule."—It will be obvious from the foregoing paragraphs that the complete and easy separation of isotopes is not as yet an accomplished fact. Theoretically, tolerably good

separations of isotopic elements may in some cases be expected, but actual experiment, and the difficulties to be surmounted during the process, indicate that a complete separation is at present only an idealistic state.

The discovery of the existence of isotopes, however, marks a great advance in the progress of physical science towards elucidating the eternal question of the constitution of matter. Especially an important generalisation resulting from the isotope theory is the rather prematurely termed "Whole-Number Rule." Before discussing this rule, however, we may with advantage turn to the efforts of William Prout, who in the early 'teens of the last century put forward a theory of the genesis and constitution of the elementary bodies. Prout's theory had its basis on the observations that that the atomic weights of the elements were represented by whole-numbers, and therefore multiples of the atomic weight of hydrogen. Hence, inferred Prout, all the elements could be conveniently regarded as condensation products of hydrogen—a view which reconciled him with the primordial matter of the ancient philosophers.

Subsequently, however, it was shown by the most accurate determinations possible that the atomic weights of many elements were not multiples of the atomic weight of hydrogen, and could not be expressed in whole-numbers. (It was also noticed afterwards that the tendency for the atomic weight of an element to deviate from a whole-number increased as the atomic weight of the element increased). Although Prout's hypothesis, as it was called, attracted many followers, no doubt on account of its simplicity, the deviation of the atomic weights of many elements from whole-numbers led to its gradual abandonment, and eventually it was relegated to the background of phlogistonism and other fallen idols of science.

The determination of the mass of isotopic elements, however, has forcibly resurrected the principle of Prout's theory. It is a remarkable fact that determinations of the atomic weight of isotopes all yield, without exception, *whole-numbers*. Should this apparent whole-number rule stand when applied to the atomic weights of further isotopes, another forward step in the elucidation of the general structure of the elements will have resulted. Elements whose present accepted atomic weights do not approximate to whole-numbers will obviously be considered to be mixtures of isotopic elements.

To quote Ashton on the whole-number rule (*Phil. Mag.*, xxxix., 233): "It is naturally premature to state that this relation is true for all elements, but the number and variety of those already exhibiting it makes the probability of this extremely high. On the other hand, it must not be supposed that this would imply that the whole-number rule holds with mathematical exactness, but only that the approximation is of a higher order than that exhibited by the ordinary chemical combining weights and is quite close enough to allow of a theory of atomic structure far simpler than those put forward in the past; for such theories were forced to attempt the explanation of fractions which now appear to be nearly fortuitous statistical effects due to the relative quantities of the isotopic constituents."

Human ideas, it has been said, are sometimes prone to cyclic periods. Is it that we are

witnessing a return to Prout's law, in principle, if not in detail, and that all the eighty odd elements may be regarded as associations of one simple atom? Such is the general trend of ideas. How it will end, and what the outcome of it all will be, may perhaps be speculated upon. Matter, although itself intensely complex in structure, may probably be sorted out into "elements" each possessing a simple relation to one another. The final solution of that cryptogram of the elements—the Periodic Table—if not simultaneously effected by progress in this field of investigation, would follow on much more easily, if, instead of being confronted by a semi-irregular array of fractional numbers, we were able to construct a table of elements whose atomic weights could be arranged in mathematical harmony.

In conclusion, another point might also be referred to in connection with the whole-number rule for isotopes. Many of our present so-called elements exhibit atomic weights which are far from being whole-numbers. And yet the atomic weights of these elements have been determined repeatedly, and with an accuracy which is beyond all question. Provisionally granting, therefore, that the deviation in atomic weight of these elements from a whole-number is due to the presence of relative quantities of component isotopes, the question arises as to why these isotopes should always be present in the necessarily same proportions to give the "element" a constant atomic weight. Many "elements" derived from widely different localities, and during intervals of many years, exhibit an absolutely identical atomic weight (within the limits of experimental error). What underlying and unseen natural law has operated to cause the effect of the complete identity of the isotopic proportions of any one element?

Here we are confronted with another problem. As Science marches steadily forwards towards the foot of the rainbow Truth, the goal would appear to recede at almost every step taken. Every new discovery of any fundamental importance brings along with it its attendant train of more and more inexplicable laws. In the oft quoted but much criticised words of Kingsley, "Skin deep below our boasted science, we are brought up short by mystery impalpable, and by the adamant walls of transcendental forces and incomprehensible laws."

ON SODIUM PHOSPHIDE.

By E. TOMKINSON and G. BARKER.

WE have been able to find no definite reference in the literature with regard to sodium phosphide, and a query in the *CHEMICAL NEWS* (cxx., p.239) elicited no reply.

The Action of Sodium on Red Phosphorus.—

(1) Sodium and red phosphorus were observed to have no action on each other in the cold. In a hard glass tube, a bright piece of sodium was placed, and to this an equal quantity of red phosphorus was added. The two adhered together. On heating, a slight effervescence took place (probably due to traces of water on the phosphorus, as red phosphorus is generally slightly moist), and the sodium absorbed the phosphorus. At this point,

reddish yellow globules sublimed on the cool portion of the tube. On further heating, white incombustible fumes arose, which supported combustion of a splint with the green flame characteristic of phosphorus compounds. These fumes subsequently became heavier, the central portion burning with the green flame. A slight condensation of these fumes also occurred. On adding water to the cooled product (a greyish mass), a very violent action took place, together with the production of a yellow sodium flame and spontaneously inflammable PH_3 . The white fumes were metaphosphoric acid, produced by the combustion of traces of yellow phosphorus in the mass, and the red substance sublimed was probably phosphorus suboxide, formed by incomplete combustion (see Thorpe and Tutton, *Journ. Chem. Soc.*, 1890, i. 549; 1891, i. 1019). (2) A quantity of red phosphorus was gently heated in a crucible until slow combustion set in. A piece of sodium was then added, which fused and absorbed the phosphorus. On further heating, the mass became ignited with the usual yellow flame of Na, and spurted globules of molten material. The crucible was then closed to preclude the oxidation of the product. On cooling, a considerable deposit of P_2O was observed on the sides and lid of the crucible. The product was a brittle greyish glossy mass of porous structure. After freeing from a slight excess of phosphorus, the product was added to a considerable excess of cold water. An extremely vigorous reaction ensued, spontaneously inflammable PH_3 being evolved. During this reaction, the solution became turbid, due to an insoluble brown substance. The filtered solution was analysed qualitatively (see later section). On another occasion, the mass was heated to redness, with the result that the mass ignited, leaving a blackish insoluble (in HCl , H_2SO_4 , and H_2O) residue. As the vessels used were generally cracked by the heat evolved, attempts were made in a tin vessel, but in all cases the product was contaminated by tin phosphide, as shown by a test for tin in the solution produced on treating the mass with water. Owing to this property of phosphorus neither platinum or copper vessels could be used.

The Action of Sodium on Yellow Phosphorus.—(1) A mixture of equal parts of sodium and yellow phosphorus was placed in a hard glass tube, and heated. (The phosphorus was freed from water used in its storage by cautions drying on filter paper. No spontaneous ignition of the sodium then occurred, but this happened in previous experiments). The sodium and phosphorus became covered with small points of flame, and when the former fused, a violent reaction took place. On cooling, a red deposit was again observed on the cool sides of the tube; the product was a white crystalline mass, from which carbon bisulphide extracted no phosphorus. With cold water, spontaneously inflammable phosphine was evolved, accompanied by small particles of free sodium burning on the surface. A small quantity of a reddish powder also separated, which was proved to be phosphorus by its forming ortho-phosphoric acid on heating with nitric acid. The liquid was The mass was ignited, and, on cooling, a black filtered and the solution examined. (2) On adding a solution of yellow phosphorus in CS_2 to sodium, the latter became covered with a red deposit.

mass remained. This evolved non-spontaneously inflammable PH_3 with water, together with an evil-smelling hydrocarbon. The latter was probably a decomposition product of the compound C_2S_2 , obtained by the action of CS_2 on Na. The solution from the product of the reaction of red phosphorus and sodium (2) contained sodium hydrate phosphite, and orthophosphate, also that from yellow phosphorus and sodium.

We wish to record that, whilst testing for orthophosphate in the solution from (2), ammonium molybdate produced a yellow colouration on heating, and then on standing developed into a deep blue liquid. This yielded no precipitates with solutions of FeCl_3 , CaCl_2 , or MgSO_4 , but gave a white precipitate with silver nitrate solution, soluble in HNO_3 , and precipitated thence as ammonium phosphomolybdate on the addition of a nitric acid solution of ammonium molybdate. This showed it to still contain a phosphate, but not an ortho-phosphate, since Ag_3PO_4 is yellow.

The subject is being further studied. We wish to express our thanks to Mr. A. R. Gower for help and advice.

Barrow-in-Furness.
August 9, 1920.

CORRESPONDENCE.

STRUCTURE OF MATTER: ISOTOPES.

To the Editor of the Chemical News.

SIR,—The chemical properties of the elements recur periodically and their classification into groups depends upon some increment or sub-atomic part, as revealed by radio-active disintegration.

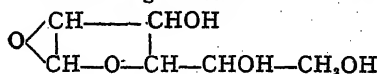
Starting with the idea that the relative quantity of the stuff (atoms) might be proportional to itself, *i.e.*, proportional to some self-determining quality as it were, say, the mass of the Rutherford outrider (or nucleus), this conception being suggested by Rutherford's famous nitrogen experiment (see CHEMICAL NEWS, 1919, cxviii, p. 311; cxx., pp. 73, 181, 193, 205, 217, 238, 291; cxxi., pp. 2, 59), by employing outriders that do not give rise to a violation of the odd-and-even-valency rule, the experimental masses can be obtained by building up the major portion of each atom with helium units (those "that help to build the atomic edifice," as implied by radio-active phenomena), round, or attached to, an "outrider."

Knowing also the soundness of the isotopic principle (now fully proved), and following up earlier ideas, published in these columns (see citations above and references therein), that all the elements with appreciable fractional atomic weights were mixtures of whole-number mass entities, *i.e.*, isotopically composite (now fully proved), it was found that in most cases the proportionate numbers of such atoms could be obtained as isotopic whole-number atoms, by cubing the mass of the outriders, which yield mean values agreeing with the experimental ones; and these were, whenever isotopes were involved, usually a little above or a little below exact whole numbers. In case the experimental value approaches the half figure (0.50) in the decimal place, the relative number of atoms to be taken is directly proportional to the masses of the outriders. Chlorine affords an example in

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxxi., No. 4.

GLUCOSANE.—M. Emile Bourquelot.—In 1860, Gélis discovered that if glucose is heated to 170° , it loses water and is converted into a brown amorphous substance which is no longer fermentable. His opinion was, that this substance was an anhydride of glucose, having the formula $C_6H_{10}O_5$, to which he gave the name glucosane, but he never isolated it in a state of purity. The above author has continued these investigations and has been able to isolate it in a chemically pure state, by slightly modifying the method adopted by Gélis. M. Bourquelot heated glucose to a temperature of 150° – 155° under a reduced pressure of 15 mm. of mercury, when water is given off, without oxidation or decomposition. On cooling an almost colourless solid is obtained. This is subjected to the action of absolute alcohol, which frees it from traces of glucose that have escaped dehydration. It is then crystallised in vacuo from a methyl alcohol solution, when colourless crystals, melting at 108° – 109° are deposited. These are pure glucosane. Analysis gives it the formula $C_6H_{10}O_5$. Glucosane is extremely hygroscopic, but it is not transformed into glucose. It cannot be distilled even in vacuo without decomposition. It is very soluble in water, fairly so in methyl alcohol and in acetic acid, slightly soluble in ethyl alcohol, and insoluble in other organic solvents. It is dextrorotatory, its rotatory value in aqueous solution is a little higher than that of glucose, and for a concentration of 3.84 per cent is equivalent to $+69.8^{\circ}$. It reduces Fehling's solution, but does not redden fuchsin solution decolorised by sulphurous acid. The most remarkable property of glucosane is its power to form additive compounds. Heated with water it is transformed into glucose. It is dissolved by hydrochloric and hydrobromic acids with the evolution of heat, and on evaporation in vacuo, halogen bodies are derived, which are very probably a chloroglucose and a bromoglucose. When dissolved in methyl alcohol saturated with hydrochloric acid gas, glucosane is converted into a methylglucoside. These reactions distinguish glucosane from its isomer levoglucosane. From pure chemical reasoning, and without taking into account stereochemistry, the author gives glucosane the following constitution—



NOTES.

IMPORTS FROM GERMANY.—The total value of imports into this country from Germany since the war amounts to £1,026,660.

The Comptroller-General of the Department of Overseas Trade informs us that an Italian firm of explosive manufacturers are engaged in

replacing much of their war and pre-war equipment by extensive coal and benzol sub-product plant, and are already turning out several lines not previously in Italy, such as phenol, saccharine, black dye, aniline, chemical manure, cinematograph films, and pure crystallised synthetic carbolic acid. The Commercial Counsellor has been informed that the company would prefer to obtain a part of the necessary machinery in Great Britain, if prices are satisfactory, and the manager would welcome catalogues and price lists of the above-mentioned plant as well as of machine tools. United Kingdom manufacturers who are interested in the foregoing and are desirous of bringing details of their manufactures to the notice of the company, will be furnished with full particulars on application to the Department of Overseas Trade, 35, Old Queen Street, S.W.1.

THE HABER DISCOVERIES IN FRANCE.—According to the *Frankfurter Zeitung* of July 25, France, at the present time, apart from her efforts in connection with the Treaty of Versailles, is desirous of obtaining the patents of the Haber process owned by the Badische Anilin und Soda Fabrik. The French Government, as agreed, has already been allowed to take over the patents registered in France, but on November 11, 1919, it entered into private negotiations with the Badische Company in connection with the acquisition of the Haber process, and the completed agreement is now awaiting the ratification of the French Senate. The French have realised that the Claude process is not altogether satisfactory, and desire to add small technical details as used in the Haber process, so that these might be put into working at a factory shortly to be erected. The proposal is to convert a powder factory at Toulouse, at present unused, and if no private company is prepared to develop the invention, under the supervision of the State, the State will do so on its own account. It is hoped eventually to manufacture in sufficient quantities to cover both military and agricultural requirements and so make France independent of other countries with regard to her supplies of ammonia.

NOTICES.

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THE CHEMICAL NEWS.

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EDITORIAL.

AS instancing the desire for research in industrial circles, the following list of Research Associations that have been formed and are in process of formation are of interest. The movement speaks well for the industries specified and incidentally should encourage the coming generation of chemists, for in practically all cases chemistry plays an important part. The young men who are at the moment filling the chemistry classes at our universities and technical colleges have a splendid future before them. The present unrest, strikes, and difficulties necessarily consequent upon the upheaval through which the world has just passed will soon be left behind, and sound common sense combined with hard work will bring its sure reward—the word for the present moment is WORK :—

- British Boot, Shoe, and Allied Trades Research Association, Technical School, Abington Square, Northampton. Secretary—Mr. John Blakeman, M.A., M.Sc.
- British Cotton Industry Research Association, 108, Deansgate, Manchester. Secretary—Miss B. Thomas.
- British Empire Sugar Research Association, Evelyn House, 62, Oxford Street, London, W.1. Secretary—Mr. W. H. Giffard.
- British Iron Manufacturers' Research Association, Atlantic Chambers, Brazenose Street, Manchester. Secretary—Mr. H. S. Knowles.
- Research Association of British Motor and Allied Manufacturers, 39, St. James's Street, London, S.W.1. Secretary—Mr. Horace Wyatt.
- British Photographic Research Association, Sicilian House, Southampton Row, London, W.C.1. Secretary—Mr. Arthur C. Brookes.
- British Portland Cement Research Association, 6, Lloyd's Avenue, London, E.C.3. Secretary—Mr. S. G. S. Panisset, A.C.G.I., F.C.S.
- British Research Association for the Woollen and Worsted Industries, Bond Place Chambers, Leeds. Secretary—Mr. Arnold Frobisher, B.Sc.
- British Scientific Instrument Research Association, 26, Russell Square, W.C.1. Secretary—Mr. J. W. Williamson, B.Sc.
- Research Association of British Rubber and Tyre Manufacturers, c/o Messrs. W. B. Peat & Co., 11, Ironmonger Lane, E.C.2.
- Linen Industry Research Association, 3, Bedford Street, Belfast. Secretary—Miss M. Burton.
- Glass Research Association, 50, Bedford Square, W.C.2. Secretary—Mr. E. Quine, B.Sc.
- British Association of Research for Cocoa, Chocolate, Sugar Confectionery, and Jam Trades, 9, Queen Street Place, E.C.4. Secretary—Mr. R. M. Leonard.
- British Non-Ferrous Metals Research Association, 29, Paradise Street, Birmingham. Secretary—Mr. E. A. Smith, A.R.S.M., M.Inst.M.M.

British Refractories Research Association, 14, Great George Street, S.W.1. Secretary—Mr. R. C. Rann.

Scottish Shale Oil Scientific and Industrial Research Association, 135, Buchanan Street, Glasgow. Secretary—Mr. W. Fraser, C.B.E.

Schemes for the establishment of Research Associations in the following industries have reached an advanced state of development :—British Music Industries Research Association, British Leather Trades Research Association, British Launderers' Research Association, British Electrical and Allied Industries Research Association, British Silk Research Association, British Motor Cycle and Cycle Car Research Association, British Cutlery Research Association, British Aircraft Research Association, Jute Spinners and Manufacturers, Grey and Malleable Cast Iron Founders, Master Bakers and Confectioners, Users of Liquid Fuels for Diesel Engines. In addition to the industries included above, certain others are engaged in the preliminary consideration of schemes for forming Research Associations.

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WILLIAM A. HERDMAN,
C.B.E., D.Sc., Sc.D., LL.D., F.R.S.,
Professor of Oceanography in the University
of Liverpool.

(Concluded from page 102).

BUT even if it be a fact that there is this alleged deficiency in tropical plankton there is by no means agreement as to the cause thereof. Brandt first attributed the poverty of the plankton in the tropics to the destruction of nitrates in the sea as a result of the greater intensity of the metabolism of denitrifying bacteria in the warmer water; and various other writers since then have more or less agreed that the presence of these denitrifying bacteria, by keeping down to a minimum the nitrogen concentration in tropical waters, may account for the relative scarcity of the phytoplankton, and consequently of the zoo-plankton, that has been observed. But Gran, Nathansohn, Murray, Hjort, and others have shown that such bacteria are rare or absent in the open sea, that their action must be negligible, and that Brandt's hypothesis is untenable. It seems clear, moreover, that the plankton does not vary directly with the temperature of the water. Furthermore, Nathansohn has shown the influence of the vertical circulation in the water upon the nourishment of the phyto-plankton—by rising currents bringing up necessary nutrient materials, and especially carbon dioxide from the bottom layers; and also possibly by conveying the products of the drainage of tropical lands to more polar seas so as to maintain the more abundant life in the colder water.

Pütter's view is that the increased metabolism in

the warmer water causes all the available food materials to be rapidly used up, and so puts a check to the reproduction of the plankton.

According to van t'Hoff's law in Chemistry, the rate at which a reaction takes place is increased by raising the temperature, and this probably holds good for all bio-chemical phenomena, and therefore for the metabolism of animals and plants in the sea. This has been verified experimentally in some cases by J. Loeb. The contrast between the plankton of Arctic and Antarctic zones, consisting of large numbers of small Crustaceans belonging to comparatively few species, and that of tropical waters, containing a great many more species generally of smaller size and fewer in number of individuals, is to be accounted for, according to Sir John Murray and others, by the rate of metabolism in the organisms. The assemblages captured in cold polar waters are of different ages and stages, young and adults of several generations occurring together in profusion, and it is supposed that the adults "may be ten, twenty, or more years of age." (Whether, however, the low temperature may not also retard reproduction is worthy of consideration). At the low temperature the action of putrefactive bacteria and of enzymes is very slow or in abeyance, and the vital actions of the Crustacea take place more slowly and the individual lives are longer. On the other hand, in the warmer waters of the tropics the action of the bacteria is more rapid, metabolism in general is more active, and the various stages in the life-history are passed through more rapidly, so that the smaller organisms of equatorial seas probably only live for days or weeks in place of years.

This explanation may account also for the much greater quantity of living organisms which has been found so often on the sea floor in polar waters. It is a curious fact that the development of the polar marine animals is in general "direct" without larval pelagic stages, the result being that the young settle down on the floor of the ocean in the neighbourhood of the parent forms, so that there come to be enormous congregations of the same kind of animal within a limited area, and the dredge will in a particular haul come up filled with hundreds, it may be, of an Echinoderm, a Sponge, a Crustacean, a Brachipod, or an Ascidian; whereas in warmer seas the young pass through a pelagic stage and so become more widely distributed over the floor of the ocean. The *Challenger* Expedition found in the Antarctic certain Echinoderms, for example, which had young in various stages of development attached to some part of the body of the parents, whereas in temperate or tropical regions the same class of animals set free their eggs and the development proceeds in the open water quite independently of, and it may be far distant from, the parent.

Another characteristic result of the difference in temperature is that the secretion of carbonate of lime in the form of shells and skeletons proceeds more rapidly in warm than in cold water. The massive shells of molluscs, the vast deposits of carbonate of lime formed by corals and by calcareous seaweeds, are characteristic of the tropics; whereas in polar seas, while the animals may be large, they are for the most part soft-bodied and destitute of calcareous secretions. The calcareous

pelagic Foraminifera are characteristic of tropical and sub-tropical plankton, and few, if any, are found in polar waters. Globigerina ooze, a calcareous deposit, is abundant in equatorial seas, while in the Antarctic the characteristic deposit is siliceous Diatomaceous ooze.

The part played by bacteria in the metabolism of the sea is very important and probably of wide-reaching effect, but we still know very little about it. A most promising young Cambridge biologist, the late Mr. G. Harold Drew, now unfortunately lost to science, had already done notable work at Jamaica and at Tortugas, Florida, on the effects produced by a bacillus which is found in the surface waters of these shallow tropical seas and in the mud at the bottom; and which denitrifies nitrates and nitrites, giving off free nitrogen. He found that this *Bacillus calcis* also caused the precipitation of soluble calcium salts in the form of calcium carbonate ("drewite") on a large scale, in the warm shallow waters. Drew's observations tend to show that the great calcareous deposits of Florida and the Bahamas previously known as "coral muds" are not, as was supposed by Murray and others, derived from broken-up corals, shells, nullipores, &c., but are minute particles of carbonate of lime which have been precipitated by the action of these bacteria (*Journ. Mar. Biol. Assoc.*, October, 1911).

The bearings of these observations upon the formation of oolitic limestones and the fine-grained unfossiliferous Lower Palæozoic limestones of New York State, recently studied in this connection by R. M. Field (Carnegie Institute of Washington, "Year Book for 1919," p. 197) must be of peculiar interest to geologists, and forms a notable instance of the annectant character of Oceanography, bringing the metabolism of living organisms in the modern sea into relation with palæozoic rocks.

The work of marine biologists on the plankton has been in the main *qualitative*, the identification of species, the observation of structure, and the tracing of life-histories. The oceanographer adds to that the *quantitative* aspect when he attempts to estimate numbers and masses per unit volume of water or of area. Let me lay before you a few thoughts in regard to some such attempts, mainly for the purpose of showing the difficulties of the investigation. Modern quantitative methods owe their origin to the ingenious and laborious work of Victor Henson, followed by Brandt, Apstein, Lohmann, and others of the Kiel school of quantitative planktologists. We may take their well-known estimations of fish eggs in the North Sea as an example of the method.

The floating eggs and embryos of our more important food fishes may occur in quantities in the plankton during certain months in spring, and Henson and Apstein have made some notable calculations based on the occurrence of these in certain hauls taken at intervals across the North Sea, which led them to the conclusion that, taking six of our most abundant fish, such as the cod and some of the flat fish, the eggs present were probably produced by about 1200 million spawners, enabling them to calculate that the total fish population of the North Sea (of these six species), at that time (spring of 1895), amounted to about 10,000 millions. Further calculations led

them to the result that the fisherman's catch of these fishes amounted to about one-quarter of the total population. Now all this is not only of scientific interest, but also of great practical importance if we could be sure that the samples upon which the calculations are based were adequate and representative, but it will be noted that these samples only represent one square metre in 3,465,968,354. Hensen's statement, repeated in various works in slightly different words, is to the effect that, using a net of which the constants are known hauled vertically through a column of water from a certain depth to the surface, he can calculate the volume of water filtered by the net and so estimate the quantity of plankton under each square metre of the surface; and his whole results depend upon the assumption, which he considers justified, that the plankton is evenly distributed over large areas of water which are under similar conditions. In these calculations in regard to the fish eggs he takes the whole of the North Sea as being an area under similar conditions, but we have known since the days of P. T. Cleve and from the observations of Hensen's own colleagues that this is not the case, and they have published chart-diagrams showing that at least three different kinds of water under different conditions are found in the North Sea, and that at least five different planktonic areas may be encountered in making a traverse from Germany to the British Isles. If the argument be used that wherever the plankton is found to vary there the conditions cannot be uniform, then few areas of the ocean of any considerable size remain as cases suitable for population-computation from random samples. It may be doubted whether even the Sargasso Sea, which is an area of more than usually uniform character, has a sufficiently evenly distributed plankton to be treated by Hensen's method of estimation of the population.

In the German Plankton Expedition of 1889, Schütt reports that in the Sargasso Sea, with its relatively high temperature, the twenty-four catches obtained were uniformly small in quantity. His analysis of the volumes of these catches shows that the average was 3.33 cc., but the individual catches ranged from 1.5 cc. to 6.5 cc., and the divergence from the average may be as great as +3.2 cc.; and, after deducting 20 per cent of the divergence as due to errors of the experiment, Schütt estimates the mean variation of the plankton at about 16 per cent above or below. This does not seem to me to indicate the uniformity that might be expected in this "halistatic" area occupying the centre of the North Atlantic Gulf Stream circulation. Hensen also made almost simultaneous hauls with the same net in quick succession to test the amount of variation, and found that the average error was about 13 per cent.

As so much depends in all work at sea upon the weather, the conditions under which the ship is working, and the care taken in the experiment, with the view of getting further evidence under known conditions I carried out some similar experiments at Port Erin on four occasions during last April and on a further occasion a month later, choosing favourable weather and conditions of tide and wind, so as to be able to maintain an approximate position. On each of four days in April the Nansen net, with No. 20 silk, was hauled

six times from the same depth (on two occasions 8 fathoms and on two occasions 20 fathoms), the hauls being taken in rapid succession and the catches being emptied from the net into bottles of 5 per cent formaline, in which they remained until examined microscopically.

The results were of interest, for although they showed considerable uniformity in the amount of the catch—for example, six successive hauls from 8 fathoms being all of them 0.2 cc., and four out of five from 20 fathoms being 0.6 cc.—the volume was made up rather differently in the successive hauls. The same organisms are present for the most part in each haul, and the chief groups of organisms are present in much the same proportion. For example, in a series where the Copepoda average about 100 the Dinoflagellates average about 300 and the Diatoms about 8000, but the percentage deviation of individual hauls from the average may be as much as *plus* or *minus* 50. The numbers for each organism (about 40) in each of the twenty-six hauls have been worked out, and the details will be published elsewhere, but the conclusion I come to is that if on each occasion one haul only, in place of six, had been taken, and if one had used that haul to estimate the abundance of any one organism in that sea-area, one might have been about 50 per cent wrong in either direction.

Successive improvements and additions to Hensen's methods in collecting plankton have been made by Lohmann, Apstein, Gran, and others, such as pumping up water of different layers through a hose-pipe and filtering it through felt, filter-paper, and other materials which retain much of the micro-plankton that escapes through the meshes of the finest silk. Use has even been made of the extraordinarily minute and beautifully regular natural filter spun by the pelagic animal *Appendicularia* for the capture of its own food. This grid-like trap, when dissected out and examined under the microscope, reveals a surprising assemblage of the smallest protozoa and protophyta, less than 30 micro-millimetres in diameter, which would all pass easily through the meshes of our finest silk nets.

The latest refinement in capturing the minutest-known organisms of the plankton (excepting the bacteria) is a culture method devised by Dr. E. J. Allen, Director of the Plymouth Laboratory (*Journ. Mar. Biol. Assoc.*, July, 1919, xii., 1). By diluting half a cubic centimetre of the seawater with a considerable amount (1500 cc.) of sterilised water treated with a nutrient solution, and distributing that over a large number (70) of small flasks in which after an interval of some days the number of different kinds of organisms which had developed in each flask were counted, he calculates that the sea contains 464,000 of such organisms per litre; and he gives reasons why his cultivations must be regarded as minimum results, and states that the total per litre may well be something like a million. Thus every new method devised seems to multiply many times the probable total population of the sea. As further results of the quantitative method it may be recorded that Brandt found about 200 diatoms per drop of water in Kiel Bay, and Hensen estimated that there are several hundred millions of diatoms under each square metre of the North Sea or the Baltic. It has been calculated that there is

approximately one Copepod in each cubic inch of Baltic Water, and that the annual consumption of the Copepoda by herring is about a thousand billion; and that in the 16 square miles of a certain Baltic fishery there is Copepod food for over 530 millions of herring of an average weight of 60 grms.

There are many other problems of the plankton in addition to quantitative estimates—probably some that we have not yet recognised—and various interesting conclusions may be drawn from recent planktonic observations. Here is a case of the introduction and rapid spread of a form new to British seas.

Biddulphia sinensis is an exotic diatom which, according to Ostenfeld, made its appearance at the mouth of the Elbe in 1903, and spread during successive years in several directions. It appeared suddenly in our plankton gatherings at Port Erin in November, 1909, and has been present in abundance each year since. Ostenfeld, in 1908, when tracing its spread in the North Sea, found that the migration to the north along the coast of Denmark to Norway corresponded with the rate of flow of the Jutland current to the Skager Rak—viz., about 17 cm. per second—a case of plankton distribution throwing light on hydrography—and he predicted that it would soon be found in the English Channel. Dr. Marie Lebour, who recently examined the store of plankton gatherings at the Plymouth Laboratory, finds that as a matter of fact this form did appear in abundance in the collections of October, 1909, within a month of the time when according to our records it reached Port Erin. Whether or not this is an Indo-Pacific species brought accidentally by a ship from the Far East, or whether it is possibly a new mutation which appeared suddenly in our seas, there is no doubt that it was not present in our Irish Sea plankton gatherings previous to 1909, but has been abundant since that year, and has completely adopted the habits of its English relations—appearing with *B. mobilensis* in late autumn, persisting during the winter, reaching a maximum in spring, and dying out before summer.

The Nauplius and Cypris stages of *Balanus* in the plankton form an interesting study. The adult barnacles are present in enormous abundance on the rocks round the coast, and they reproduce in winter, at the beginning of the year. The newly emitted young are sometimes so abundant as to make the water in the shore pools and in the sea close to the shore appear muddy. The Nauplii first appeared at Port Erin, in 1907, in the bay gatherings on February 22 (in 1908 on February 13), and increased with ups and down to their maximum on April 15, and then decreased until their disappearance on April 26. None were taken at any other time of the year. The cypris stage follows on after the Nauplius. It was first taken in the bay on April 6, rose to its maximum on the same day with the Nauplii, and was last caught on May 24. Throughout, the Cypris curve keeps below that of the Nauplius, the maxima being 1740 and 10,500 respectively. Probably the difference between the two curves represents the death-rate of *Balanus* during the Nauplius stage. That conclusion I think we are justified in drawing, but I would not venture to use the result of any haul, or the average of a number of hauls,

to multiply by the number of square yards in a zone round our coast in order to obtain an estimate of the number of young barnacles, or of the old barnacles that produced them—the irregularities are too great.

To my mind it seems clear that there must be three factors making for irregularity in the distribution of a plankton organism:—

1. The sequence of stages in its life-history—such as the Nauplius and Cypris stages of *Balanus*.

2. The results of interaction with other organisms—as when a swarm of *Calanus* is pursued and devoured by a shoal of herring.

3. Abnormalities in time or abundance due to the physical environment—as in favourable or unfavourable seasons.

And these factors must be at work in the open ocean as well as in coastal waters.

In many oceanographical inquiries there is a double object. There is the scientific interest and there is the practical utility—the interest, for example, of tracing a particular swarm of a Copepod like *Calanus*, and of making out why it is where it is at a particular time, tracing it back to its place of origin, finding that it has come with a particular body of water, and perhaps that it is feeding upon a particular assemblage of Diatoms; endeavouring to give a scientific explanation of every stage in its progress. Then there is the utility—the demonstration that the migration of the *Calanus* has determined the presence of a shoal of herrings or mackerel that are feeding upon it, and so have been brought within the range of the fisherman and have constituted a commercial fishery.

We have evidence that pelagic fish which congregate in shoals, such as herring and mackerel, fed upon the Crustacea of the plankton and especially upon Copepoda. A few years ago when the summer herring fishery off the south end of the Isle of Man was unusually near the land, the fishermen found large red patches in the sea where the fish were specially abundant. Some of the red stuff, brought ashore by the men, was examined at the Port Erin Laboratory and found to be swarms of Copepod *Temora longicornis*; and the stomachs of the herring caught at the same time were engorged with the same organism. It is not possible to doubt that during these weeks of the herring fishery in the Irish Sea the fish were feeding mainly upon this species of Copepod. Some ten years ago, Dr. E. J. Allen and Mr. G. E. Bullen published some interesting work (*Journ. Mar. Biol. Assoc.*, 1909, viii., pp. 394-406), from the Plymouth Marine Laboratory, demonstrating the connection between mackerel and Copepoda and sunshine in the English Channel; and Farran (*Conseil Internat. Bull. Trimestr.*, 1902-8, "Planktonique," p. 89) states that in the spring fishery on the West of Ireland the food of the mackerel is mainly composed of *Calanus*.

Then again at the height of the summer mackerel fishery in the Hebrides, in 1913, we found ("Spoila Runiana," iii., *Linn. Soc. Journ., Zoology*, 1918, xxxiv., p. 95) the fish feeding upon the large Copepod *Calanus finmarchicus*, which was caught in the tow-net at the rate of about 6000 in a five minutes' haul, and 6000 was also the average number found in the stomachs of the fish caught at the same time.

These were cases where the fish were feeding upon the organism that was present in swarms—a monotonic plankton—but in other cases the fish are clearly selective in their diet. If the sardine of the French coast can pick out from the micro-plankton the minute Peridiniales in preference to the equally minute Diatoms which are present in the sea at the same time, there seems no reason why the herring and the mackerel should not be able to select particular species of Copepoda or other large organisms from the macro-plankton, and we have evidence that they do. Nearly thirty years ago the late Mr. Isaac Thompson, a constant supporter of the Zoological Section of this Association and one of the Honorary Local Secretaries for the last Liverpool meeting, showed me in 1893 that young plaice at Port Erin were selecting one particular Copepod, a species of *Jonesiella*, out of many others caught in our tow-nets at the time. H. Blegvad (*Rep. Danish Biol. Stat.*, 1916, xxiv.) showed in 1916 that young food fishes and also small shore fishes pick out certain species of Copepoda (such as Harpacticoids) and catch them individually—either lying in wait or searching for them. A couple of years later, Dr. Marie Lebour published a detailed account of her work at Plymouth on the food of young fishes (*Journal. Mar. Biol. Assoc.*, May, 1918), proving that certain fish undoubtedly do prefer certain planktonic food.

These Crustacea of the plankton feed upon smaller and simpler organisms—the Diatoms, the Peridinians, and the Flagellates—and the fish themselves in their youngest post-larval stages are nourished by the same minute forms of the plankton. Thus it appears that our sea-fisheries ultimately depend upon the living plankton which no doubt in its turn is affected by hydrographic conditions. A correlation seems to be established between the Cornish pilchard fisheries and periodic variations in the physical characters (probably the salinity) of the water of the English Channel between Plymouth and Jersey (see E. C. Jee, *Hydrography of the English Channel*, 1904-17). Apparently a diminished intensity in the Atlantic current corresponds with a diminished fishery in the following summer. Possibly the connection in these cases is through an organism of the plankton.

It is only a comparatively small number of different kinds of organisms—both plants and animals—that make up the bulk of the plankton that is of real importance to fish. One can select about half-a-dozen species of Copepoda which constitute the greater part of the summer zooplankton suitable as food for larval or adult fishes, and about the same number of generic types of Diatoms which similarly make up the bulk of the available spring phyto-plankton year after year. This fact gives great economic importance to the attempt to determine with as much precision as possible the times and conditions of occurrence of these dominant factors of the plankton in an average year. An obvious further extension of this investigation is an enquiry into the degree of coincidence between the times of appearance in the sea of the plankton organisms and of the young fish, and the possible effect of any marked absence of correlation in time and quantity.

Just before the war the International Council for the Exploration of the Sea (*Rapports et Proc.*

Verb., December, 1913, xix.) arrived at the conclusion that fishery investigations indicated the probability that the great periodic fluctuations in the fisheries are connected with the fish larvæ being developed in great quantities only in certain years. Consequently they advised that plankton work should be directed primarily to the question whether these fluctuations depend upon differences in the plankton production in different years. It was then proposed to begin systematic investigation of the fish larvæ and the plankton in spring and to determine more definitely the food of the larval fish at various stages.

About the same time Dr. Hjort (*Rapports et Proc. Verb.*, 1914, xx., 204) made the interesting suggestion that possibly the great fluctuations in the number of young fish observed from year to year may not depend wholly upon the number of eggs produced, but also upon the relation in time between the hatching of these eggs and the appearance in the water of the enormous quantity of Diatoms and other plant plankton upon which the larval fish after the absorption of their yolk depend for food. He points out that, if even a brief interval occurs between the time when the larvæ first require extraneous nourishment and the period when such food is available, it is highly probable that an enormous mortality would result. In that case even a rich spawning season might yield but a poor result in fish in the commercial fisheries of successive years for some time to come. So that, in fact, the numbers of a year-class may depend not so much upon a favourable spawning season as upon a coincidence between the hatching of the larvæ and the presence of abundance of phyto-plankton available as food. (For the purpose of this argument we may include in "phyto-plankton" the various groups of Flagellata and other minute organisms which may be present with the Diatoms).

The curve for the spring maximum of Diatoms corresponds in a general way with the curve representing the occurrence of pelagic fish eggs in our seas. But is the correspondence sufficiently exact and constant to meet the needs of the case? The phyto-plankton may still be relatively small in amount during February and part of March in some years, and it is not easy to determine exactly when, in the open sea, the fish eggs have hatched out in quantity and the larvæ have absorbed their food-yolk and started feeding on Diatoms.

If, however, we take the case of one important fish—the plaice—we can get some data from our hatching experiments at the Port Erin Biological Station which have now been carried on for a period of seventeen years. An examination of the hatchery records for these years in comparison with the plankton records of the neighbouring sea, which have been kept systematically for the fourteen years from 1907 to 1920 inclusive, shows that in most of these years the Diatoms were present in abundance in the sea a few days at least before the fish larvæ from the hatchery were set free, and that it was only in four years (1908, 1909, 1913, and 1914) that there was apparently some risk of the larvæ finding no phyto-plankton food, or very little. The evidence so far seems to show that if fish larvæ are set free in the sea as late as March 20, they are fairly sure of finding suitable food; but if they are hatched as early as February they run some chance of being starved.

(All dates and statements as to occurrence refer to the Irish Sea round the south end of the Isle of Man. For further details see *Report Lancs. Sea-Fish. Lab.* for 1919).

But this does not exhaust the risks to the future fishery. C. G. Joh. Petersen and Boysen-Jensen in their valuation of the Limfjord (*Report of Danish Biol. Station* for 1919) have shown that in the case not only of some fish but also of the larger invertebrates on which they feed there are marked fluctuations in the number of young produced in different seasons, and that it is only at intervals of years that a really large stock of young is added to the population.

The prospects of a year's fishery may therefore depend primarily upon the rate of spawning of the fish, affected no doubt by hydrographic and other environmental conditions, secondarily upon the presence of a sufficient supply of phytoplankton in the surface layers of the sea at the time when the fish larvae are hatched, and that in its turn depends upon photosynthesis and physico-chemical changes in the water, and finally upon the reproduction of the stock of molluscs or worms at the bottom which constitute the fish food at later stages of growth and development.

The question has been raised of recent years—Is there enough plankton in the sea to provide sufficient nourishment for the larger animals, and especially for those fixed forms such as sponges that are supposed to feed by drawing currents of plankton-laden water through the body? In a series of remarkable papers from 1907 onwards Pütter and his followers put forward the views (1) that the carbon requirements of such animals could not be met by the amount of plankton in the volume of water that could be passed through the body in a given time, and (2) that sea-water contained a large amount of dissolved organic carbon compounds which constitute the chief if not the only food of a large number of marine animals. These views have given rise to much controversy and have been useful in stimulating further research, but I believe it is now admitted that Pütter's samples of water from the Bay of Naples and at Kiel were probably polluted, that his figures were erroneous, and that his conclusions must be rejected, or at least greatly modified. His estimates of the plankton were minimum ones, while it seems probable that his figures for the organic carbon present represent a variable amount of organic matter arising from one of the reagents used in the analyses (see Moore, etc., *Bio-Chem. Journ.*, 1912, vi., 266). The later experimental work of Henze, of Raben, and of Moore shows that the organic carbon dissolved in sea-water is an exceedingly minute quantity, well within the limits of experimental error. Moore puts it, at the most, at one-millionth part, or 1 mgrm. in a litre. At the Dundee meeting of the Association in 1912, a discussion on this subject took place, at which Pütter still adhered to a modified form of his hypothesis of the inadequacy of the plankton and the nutrition of lower marine animals by the direct absorption of dissolved organic matter. Further work at Port Erin since has shown that, while the plankton supply as found generally distributed would prove sufficient for the nutrition of such sedentary animals as Sponges and Ascidians, which require to filter only about fifteen times their own volume of

water per hour, it is quite inadequate for active animals such as Crustaceans and Fishes. These latter are, however, able to seek out and capture their food, and are not dependent on what they may filter or absorb from the sea-water. This result accords well with recorded observations on the irregularity in the distribution of the plankton, and with the variations in the occurrence of the migratory fishes which may be regarded as following and feeding upon the swarms of planktonic organisms.

This then, like most of the subjects I am dealing with, is still a matter of controversy, still not completely understood. Our need, then, is Research, more Research, and *still more Research*.

Our knowledge of the relations between plankton productivity and variation and the physico-chemical environment is still in its infancy, but gives promise of great results in the hands of the bio-chemist and the physical chemist.

Recent papers by Sorensen, Palitzsch, Witting, Moore, and others have made clear that the amount of hydrogen-ion concentration as indicated by the relative degree of alkalinity and acidity in the sea-water may undergo local and periodic variations and that these have an effect upon the living organisms in the water and can be correlated with their presence and abundance. To take an example from our own seas, Professor Benjamin Moore and his assistants in their work at the Port Erin Biological Station in successive years from 1912 onwards have shown ("Photosynthetic phenomena in sea-water," *Liverpool Biol. Soc.*, 1915, xxix., 233) that the sea around the Isle of Man is a good deal more alkaline in spring (say April) than it is in summer (say July). The alkalinity, which gets low in summer, increases somewhat in autumn, and then decreases rapidly, to disappear during the winter; and then once more, after several months of a minimum, begins to come into evidence again in March, and rapidly rises to its maximum in April or May. This periodic change in alkalinity will be seen to correspond roughly with the changes in the living microscopic contents of the sea represented by the phyto-plankton annual curve, and the connection between the two will be seen when we realise that the alkalinity of the sea is due to the relative absence of carbon dioxide. In early spring, then, the developing myriads of diatoms in their metabolic processes gradually use up the store of carbon dioxide accumulated during the winter, or derived from the bi-carbonates of calcium and magnesium, and so increase the alkalinity of the water, till the maximum of alkalinity due to the fixation of the carbon and the reduction in amount of carbon dioxide, corresponds with the crest of the phyto-plankton curve in, say, April. Moore has calculated that the annual turnover in the form of carbon which is used up or converted from the inorganic into an organic form probably amounts to something of the order of 20,000 or 30,000 tons of carbon per cubic mile of sea-water, or, say, over an area of the Irish Sea measuring 16 square miles and a depth of 50 fathoms; and this probably means a production each season of about two tons of dry organic matter, corresponding to at least ten tons of moist vegetation, per acre—which suggests that we may still be very far from getting from our seas anything like the amount of possible food-matters that are produced annually.

Testing the alkalinity of the sea-water may therefore be said to be merely ascertaining and measuring the results of the photosynthetic activity of the great phyto-plankton rise in spring due to the daily increase of sunlight.

The Marine biologists of the Carnegie Institute, Washington, have made a recent contribution to the subject in certain observations on the alkalinity of the sea (as determined by hydrogen-ion concentration), during which they found in tropical mid-Pacific a sudden change to acidity in a current running eastwards. Now in the Atlantic the Gulf Stream, and tropical Atlantic Waters generally, are much more alkaline than the colder coastal water running south from the Gulf of St. Lawrence. That is, the colder Arctic water has more carbon dioxide. This suggests that the Pacific easterly set may be due to deeper water, containing more carbon dioxide (=acidity), coming to the surface at that point. The alkalinity of the sea-water can be determined rapidly by mixing the sample with a few drops of an indicator and observing the change of colour; and this method of detecting ocean currents by observing the hydrogen-ion concentration of the water might be useful to navigators as showing the time of entrance to a known current.

Oceanography has many practical applications—chiefly, but by no means wholly, on the biological side. The great fishing industries of the world deal with living organisms, of which all the vital activities and the inter-relations with the environment are matters of scientific investigation. Aquiculture is as susceptible of scientific treatment as agriculture can be; and the fisherman who has been in the past too much the nomad and the hunter—if not, indeed, the devastating raider—must become in the future the settled farmer of the sea if his harvest is to be less precarious. Perhaps the nearest approach to cultivation of a marine product, and of the fisherman reaping what he has actually sown, is seen in the case of the oyster and mussel industries on the west coast of France, in Holland, America, and to a less extent on our own coast. Much has been done by scientific men for these and other similar coastal fisheries since the days when Professor Coste in France in 1859 introduced oysters from the Scottish oyster-beds to start the great industry at Arcachon and elsewhere. Now we buy back the descendants of our own oysters from the French ostreiculturists to replenish our depleted beds.

It is no small matter to have introduced a new and important food-fish to the markets of the world. The remarkable deep-water "tile-fish," new to science and described as *Lopholatilus chamaeleonticeps*, was discovered in 1879 by one of the United States fishing schooners to the south of Nantucket, near the 100-fathom line. Several thousand pounds weight were caught, and the matter was duly investigated by the United States Fish Commission. For a couple of years after that the fish was brought to market in quantity, and then something unusual happened at the bottom of the sea, and in 1882 millions of dead tile-fish were found floating on the surface over an area of thousands of square miles. The schooner *Navarino* sailed for two days and a night through at least 150 miles of sea, thickly covered as far as the eye could reach with dead fish, estimated at 256,000 to the square mile. The Fish

Commission sent a vessel to fish systematically over the grounds known as the "Gulf Stream slope," where the tile-fish had been so abundant during the two previous years, but she did not catch a single fish, and the associated sub-tropical invertebrate fauna was also practically obliterated.

This wholesale destruction was attributed by the American oceanographers to a sudden change in the temperature of the water at the bottom, due in all probability to a withdrawal southwards of the warm Gulf Stream water and a flooding of the area by the cold Labrador current.

I am indebted to Dr. C. H. Townsend, Director of the celebrated New York Aquarium, for the latest information in regard to the reappearance in quantity of this valuable fish upon the old fishing grounds off Nantucket and Long Island, at about 100 miles from the coast to the east and south-east of New York. It is believed that the tile-fish is now abundant enough to maintain an important fishery, which will add an excellent food-fish to the markets of the United States. It is easily caught with lines at all seasons of the year, and reaches a length of over three feet and a weight of 40 to 50 pounds. During July, 1915, the product of the fishery was about two-and-a-half million pounds weight, valued at 55,000 dollars, and in the first few months of 1917 the catch was four-and-a-half million pounds, for which the fishermen received 247,000 dollars.

We can scarcely hope in European seas to add new food-fishes to our markets, but much may be done through the co-operation of scientific investigators of the ocean with the Administrative Departments to bring about a more rational conservation and exploitation of the national fisheries.

Earlier in this address I referred to the pioneer work of the distinguished Manx naturalist, Professor Edward Forbes. There are many of his writings and of his lectures which I have no space to refer to which have points of oceanographic interest. Take this, for example, in reference to our national sea fisheries. We find him in 1847 writing to a friend: "On Friday night I lectured at the Royal Institution. The subject was the bearing of submarine researches and distribution matters on the fishery question. I pitched into Government mismanagement pretty strong, and made a fair case of it. It seems to me that at a time when half the country is starving we are utterly neglecting or grossly mismanaging great sources of wealth and food. . . . Were I a rich man I would make the subject a hobby, for the good of the country and for the better proving that the true interests of Government are those linked with and inseparable from Science." We must still cordially approve of these last words, while recognising that our Government Department of Fisheries is now being organised on better lines, is itself carrying on scientific work of national importance, and is, I am happy to think, in complete sympathy with the work of independent scientific investigators of the sea and desirous of closer co-operation with University laboratories and biological stations.

During recent years one of the most important and most frequently discussed of applications of fisheries investigation has been the productivity of the trawling grounds, and especially those of

the North Sea. It has been generally agreed that the enormous increase of fishing power during the last forty years or so has reduced the number of large plaice, so that the average size of that fish caught in our home waters has become smaller, although the total number of plaice landed had continued to increase up to the year of the outbreak of war. Since then, from 1914 to 1919, there has of necessity been what may be described as the most gigantic experiment ever seen in the closing of extensive fishing grounds. It is still too early to say with any certainty exactly what the results of that experiment have been, although some indications of an increase of the fish population in certain areas have been recorded. For example, the Danes, A. C. Johansen and Kirstine Smith, find that large plaice landed in Denmark are now more abundant, and they attribute this to a reversal of the pre-war tendency, due to less intensive fishing. But Dr. James Johnstone has pointed out that there is some evidence of a natural periodicity in abundance of such fish and that the results noticed may represent phases in a cyclic change. If the periodicity noted in Liverpool Bay (see Johnstone, *Report Lancs. Sea-Fish. Lab.* for 1917, p. 60; and Daniel, *Report* for 1919, p. 51) holds good for other grounds it will be necessary in any comparison of pre-war and post-war statistics to take this natural variation in abundance into very careful consideration.

In the application of oceanographic investigations to sea-fisheries problems, one ultimate aim, whether frankly admitted or not, must be to obtain some kind of a rough approximation to a census or valuation of the sea—of the fishes that form the food of man, of the lower animals of the sea-bottom on which many of the fishes feed, and of the planktonic contents of the upper waters which form the ultimate organised food of the sea—and many attempts have been made in different ways to attain the desired end.

Our knowledge of the number of animals living in different regions of the sea is for the most part relative only. We know that one haul of the dredge is larger than another, or that one locality seems richer than another, but we have very little information as to the actual numbers of any kind of animal per square foot or per acre in the sea. Hensen, as we have seen, attempted to estimate the number of food-fishes in the North Sea from the number of their eggs caught in a comparatively small series of hauls of the tow-net, but the data were probably quite insufficient and the conclusions may be erroneous. It is an interesting speculation to which we cannot attach any economic importance. Heincke says of it: "This method appears theoretically feasible, but presents in practice so many serious difficulties that no positive results of real value have as yet been obtained."

All biologists must agree that to determine even approximately the number of individuals of any particular species living in a known area is a contribution to knowledge which may be of great economic value in the case of the edible fishes, but it may be doubted whether Hensen's methods, even with greatly increased data, will ever give us the required information. Petersen's method, of setting free marked plaice and then assuming that the proportion of these recaptured is to the total number marked as the fishermen's catch in the same dis-

trict is to the total population, will only hold good in circumscribed areas where there is practically no migration and where the fish are fairly evenly distributed. This method gives us what has been called "the fishing coefficient," and this has been estimated for the North Sea to have a probable value of about 0.33 for those sizes of fish which are caught by the trawl. Heincke (F. Heincke, *Cons. Per. Internat. Explor. de la Mer*, "Investigations on the Plaice," Copenhagen, 1913), from an actual examination of samples of the stock on the ground obtained by experimental trawling ("the catch coefficient"), supplemented by the market returns of the various countries, estimates the adult plaice at about 1,500 millions, of which about 500 millions are caught or destroyed by the fishermen annually.

It is difficult to imagine any further method which will enable us to estimate any such case as, say, the number of plaice in the North Sea where the individuals are so far beyond our direct observation and are liable to change their positions at any moment. But a beginning can be made on more accessible ground with more sedentary animals, and Dr. C. G. Joh. Petersen, of the Danish Biological Station, has for some years been pursuing the subject in a series of interesting Reports on the "Evaluation of the Sea" (see *Reports of the Danish Biological Station*, and especially the *Report* for 1918 "The Sea Bottom and its Production of Fish Food"). He uses a bottom-sampler, or grab, which can be lowered down open and then closed on the bottom so as to bring up a sample square foot or square metre (or in deep water one-tenth of a square metre) of the sand or mud and its inhabitants. With this apparatus, modified in size and weight for different depths and bottoms, Petersen and his fellow-workers have made a very thorough examination of the Danish waters, and especially of the Kattegat and the Limfjord, have described a series of "animal communities" characteristic of different zones and regions of shallow water, and have arrived at certain numerical results as to the quantity of animals in the Kattegat expressed in tons—such as 5000 tons of plaice requiring as food 50,000 tons of "useful animals" (mollusca and polychaet worms), and 25,000 tons of starfish using up 200,000 tons of useful animals which might otherwise serve as food for fishes, and the dependence of all these animals directly or indirectly upon the great Beds of *Zostera*, which makes up 24,000,000 tons in Kattegat. Such estimates are obviously of great biological interest, and even if only rough approximations, are a valuable contribution to our understanding of the metabolism of the sea and of the possibility of increasing the yield of local fisheries.

But on studying these Danish results in the light of what we know of our own marine fauna, although none of our seas have been examined in the same detail by the bottom-sampler method, it seems probable that the animal communities as defined by Petersen are not exactly applicable on our coasts and that the estimates of relative and absolute abundance may be very different in different seas under different conditions. The work will have to be done in each great area, such as the North Sea, the English Channel, and the Irish Sea, independently. This is a necessary investigation, both biological and physical, which

lies before the oceanographers of the future, upon the results of which the future preservation and further cultivation of our national sea-fisheries may depend.

It has been shown by Johnstone and others that the common edible animals of the shore may exist in such abundance that an area of the sea may be more productive of food for man than a similar area of pasture or crops on land. A Lancashire mussel bed has been shown to have as many as 16,000 young mussels per square foot, and it is estimated that in the shallow waters of Liverpool Bay there are from 20 to 200 animals of sizes varying from an amphipod to a plaice on each square metre of the bottom (*Conditions of Life in the Sea*, Cambridge Univ. Press, 1908).

From these and similar data which can be readily obtained, it is not difficult to calculate totals by estimating the number of square yards in areas of similar character between tide-marks or in shallow water. And from weighings of samples some approximation to the number of tons of available food may be computed. But one must not go too far. Let all the figures be based upon actual observation. Imagination is necessary in science, but in calculating a population of even a very limited area it is best to believe only what one can see and measure.

Countings and weighings, however, do not give us all the information we need. It is something to know approximately the number of millions of animals on a mile of shore and the number of millions of tons of possible food in a sea-area, but that is not sufficient. All food-fishes are not equally nourishing to man, and all plankton and bottom invertebrata are not equally nourishing to a fish. At this point the biologist requires the assistance of the physiologist and the bio-chemist. We want to know next the value of our food matters in proteids, carbohydrates, and fats, and the resulting calories. Dr. Johnstone, of the Oceanography Department of the University of Liverpool, has already shown us how markedly a fat summer herring differs in essential constitution from the ordinary white fish, such as the cod, which is almost destitute of fat.

Professor Brandt, at Kiel, Professor Benjamin Moore, at Port Erin, and others have similarly shown that plankton gatherings may vary greatly in their nutrient value according as they are composed mainly of Diatoms, of Dinoflagellates, or of Copepoda. And, no doubt, the animals of the "benthos," the common invertebrates of our shores, will show similar differences in analysis.* It is obvious that some contain more solid flesh, others more water in their tissues, others more calcareous matter in the exoskeleton, and that therefore weight for weight we may be sure that some are more nutritious than the others; and this is probably at least one cause of that preference we see in some of our bottom-feeding fish for certain kinds of food, such as polychaet worms, in which there is relatively little waste, and thin-shelled lamellibranch molluscs, such as young mussels, which have a highly nutrient body in a comparatively thin and brittle shell.

* Moore and others have made analyses of the protein, fat, etc., in the soft parts of Sponge, Ascidian, Pylisia, Fusus, Echinus, and Cancer at Port Erin, and find considerable differences—the protein ranging, for example, from 8 to 51 per cent, and the fat from 2 to 14 per cent (see *Bio-Chemical Journ.* vi. p. 292).

My object in referring to these still incomplete investigations is to direct attention to what seems a natural and useful extension of faunistic work, for the purpose of obtaining some approximation to a quantitative estimate of the more important animals of our shores and shallow water and their relative values as either the immediate or the ultimate food of marketable fishes.

Each such fish has its "food-chain" or series of alternative chains, leading back from the food of man to the invertebrates upon which it preys and then to the food of these, and so down to the smallest and simplest organisms in the sea, and each such chain must have all its links fully worked out as to seasonal and quantitative occurrence back to the Diatoms and Flagellates which depend upon physical conditions and take us beyond the range of biology—but not beyond that of oceanography. The Diatoms and the Flagellates are probably more important than the more obvious sea-weeds not only as food, but also in supplying to the water the oxygen necessary for the respiration of living protoplasm. Our object must be to estimate the rate of production and rate of destruction of all organic substances in the sea.

To attain to an approximate census and valuation of the sea—remote though it may seem—is a great aim, but it is not sufficient. We want not only to observe and to count natural objects, but also to understand them. We require to know not merely what an organism is—in the fullest detail of structure and development and affinities—and also where it occurs—again in full detail—and in what abundance under different circumstances, but also *how* it lives and what all its relations are to both its physical and its biological environment, and that is where the physiologist and especially the bio-chemist, can help us. In the best interests of biological progress the day of the naturalist who merely collects, the day of the anatomist and histologist who merely describe, is over, and the future is with the observer and the experimenter animated by a divine curiosity to enter into the life of the organism and understand how it lives and moves and has its being. "Happy indeed is he who has been able to discover the causes of things."

Cardiff is a sea-port, and a great sea-port, and the Bristol Channel is a notable sea-fisheries centre of growing importance. The explorers and merchant venturers of the South-West of England are celebrated in history. What are you doing now in Cardiff to advance our knowledge of the ocean? You have here an important university centre and a great modern national museum, and either or both of these homes of research might do well to establish an oceanographical department, which would be an added glory to your city and of practical utility to the country. This is the obvious centre in Wales for a sea-fisheries institute for both research and education. Many important local movements have arisen from British Association meetings, and if such a notable scientific development were to result from the Cardiff meeting of 1920, all who value the advance of knowledge and the application of knowledge to industry would applaud your enlightened action.

But in a wider sense, it is not to the people of Cardiff alone that I appeal, but to the whole population of these Islands, a maritime people

who owe everything to the sea. I urge them to become better informed in regard to our national sea-fisheries and take a more enlightened interest in the basal principles that underlie rational regulation and exploitation of these important industries. National efficiency depends to a very great extent upon the degree in which scientific results and methods are appreciated by the people and scientific investigation is promoted by the Government and other administrative authorities. The principles and discoveries of science apply to aquiculture no less than to agriculture. To increase the harvest of the sea the fisheries must be continuously investigated, and such cultivation as is possible must be applied, and all this is clearly a natural application of the biological and hydrographical work now united under the science of Oceanography.

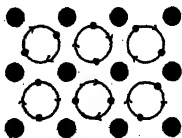
CORRESPONDENCE.

ELECTRONS AND NUCLEI.

To the Editor of the Chemical News.

SIR,—The idea that the electrons revolve round the positive nuclei as central suns, according to the Bohr-Rutherford atom theory, is supported by much evidence; but when one considers an assemblage of nuclei as in either an atom structure or a crystal structure, more or less complex, certain difficulties seem to present themselves.

Without going into all the "pros and cons," it seems worth while considering the electrons arranged in *pairs*, as in the accompanying diagram (taken as a plan view), and revolving as shown when certain conditions are impressed upon the assemblage. Just what these conditions would be it is difficult to say, but there appears to be no reason why this arrangement should not be a stable one when all the electro-dynamic consequences, as involved in a three-dimensional structure, are worked out.



A sectional elevation view would show the linking up of the nuclei by lines of force (bonds) emanating from each negative electron. Each pair of electrons would be common to two nuclei situated at opposite ends of the axis of rotation. Each axis might represent a line of magnetic force so that if all the electron pairs were revolving in the same direction the axial lines would be extended and a magnetic state would be represented. In the diagram the large black dots represent the positive nuclei.—I am, &c.,

F. H. LORING.

NOTES.

INSTITUTE OF METALS. — *Autumn Meeting, Barrow-in-Furness, September 15 and 16, 1920.*—The following is a list of the Papers that are expected to be submitted:—

- W. E. Alkins, M.Sc. (Manchester), on "The Immiscibility of Metals from the Point of View of the Phase Rule."
 Engineer Lieutenant-Commander G. B. Allen, R.N. (London), on "Service Experience with Condensers."
 T. G. Bamford, M.Sc. (Birmingham), and W. E. Ballard (Birmingham), on "The Influence of Gases on High-Grade Brass."
 Kathleen E. Bingham, B.Sc. (Teddington), on "The Allotropy of Zinc."
 Professor H. C. H. Carpenter, M.A., Ph.D., A.R.S.M., F.R.S. (London), and Constance F. Elam (New Barnet), on "Crystal Growth and Recrystallisation in Metals."
 J. H. S. Dickenson (Sheffield), "Note on a Failure of Manganese Bronze."
 D. Hanson, M.Sc. (Teddington), and Marie L. V. Gayler, B.Sc. (Teddington), on "The Constitution of the Alloys of Aluminium and Magnesium."
 O. F. Hudson, D.Sc. (London), and J. H. Darley (London), on "The Constitution and Structure of Certain Tin-Antimony-Copper Alloys."
 F. Johnson, M.Sc. (Birmingham), on "Some Features in the Behaviour of Beta Brass when Cold-Rolled."
 R. T. Rolfe, F.I.C. (Bedford), on "The Effect of Increasing Proportions of Antimony and of Arsenic respectively upon the Properties of Admiralty Gun-Metal."
 H. B. Weeks, F.I.C., "Notes on Brass Foundry Practice at Messrs. Vickers Limited, Barrow-in-Furness."

Members intending to take part in the discussion of any of the Papers can be supplied with a copy a week before the Meeting on application to the Secretary. Copies of all Papers will, it is hoped, be available at the Meeting for the use of Members who have not previously received copies, and those who are unable to attend will be subsequently be supplied, on application, with a copy of any Paper of which prints remain. In the Discussion following the reading of the Papers each speaker will be limited to ten minutes, unless the time should be extended by the Chairman. Speakers who are unable to give more than a summary of their views in the time available may send a written statement to the Secretary for publication in the December issue of the *Journal*, such statement to be in the hands of the Secretary not later than noon on October 16, 1920.

INSTITUTION OF MINING ENGINEERS. — The Thirty-first Annual General Meeting of the Members of the Institution of Mining Engineers will be held in the Lord Mayor's Parlour, Town Hall, Manchester, on Wednesday, September 15, 1920, at 10.30 a.m. Arrangements have been made for visits to places of interest and works on September 16 and 17. In order that the necessary arrangements may be made, members are desired to make application for tickets for the Manchester Meeting, not later than September 7, to Mr. N. T. Williams, Hon. Secretary of the Manchester Geological and Mining Society, 5, John Dalton Street, Manchester. All applications for the Dinner, Excursions, etc., received after that date will be subject to the accommodation proving sufficient. Attention of members is drawn to the desirability of increased membership, and they are urged by the President to propose suitable persons for any of the classes of membership.

ELECTRICITY METERS FOR NEW ZEALAND.—In a recent communication H.M. Trade Commissioner in New Zealand (Mr. R. Dalton) gives some particulars obtained from the Chief Electrical Engineer, Public Works Department, Wellington, on the types of meter found suitable for that market. It is stated that the maximum demand system is very suitable for hydro-electric power systems, and would have been used more widely if a cheaper and more accurate instrument were available. So far the only reasonably cheap types are wanting in accuracy. The clockwork types are too expensive. A good serviceable maximum demand indicator, costing, say, £2 to £4 without wattmeter, or £3 to £6 with wattmeter dial as well as maximum demand dial, would find a ready sale. A satisfactory commercial maximum K.V.A. meter suitable for service on demands of 5 up to 500 K.V.A. graduated for 400 volts, 3300 volts and 11,000 volts is required. So far no suitable instrument for measuring maximum K.V.A. has been available, and consequently it is necessary to take the maximum kilowatts averaged over half-an-hour and deduce therefrom the maximum K.V.A. from the power factor observed during heavy loads. This system is obviously unsatisfactory if a suitable maximum K.V.A. or maximum current measuring instrument is available. The standard frequency for New Zealand is 50 cycles. A copy of the latest scale of charges has been forwarded and may be seen by British firms on application to the Enquiry Room at the Department, at 35, Old Queen Street, quoting D.O.T./2218/ED. According to this four rates are in operation, viz., Rate A, a fixed rate for domestic and farm service; Rate B, a two-rate system for domestic purposes; Rate C, meter rate for general purposes; and Rate D, maximum demand for general purposes. Of the wholesale rates the most popular is Rate D based on maximum K.V.A. demand, and a large number of consumers will come on to this rate in the Canterbury and Waikato districts. The Chief Electrical Engineers will be glad to hear from firms offering purely British material likely to be of use for the above purposes.

ALSATIAN POTASH.—The French Minister of Agriculture, in a notice published in the *Journée Industrielle* reminds persons interested in the purchase of Alsatian potash salts that trade in this commodity is now free. He adds that orders for potash are no concern of his department, and that they should be sent either to Mulhouse, or to the various representatives to the "Société Commerciale des potasses d'Alsace." Whereas before the war the consumption of pure potash in France did not exceed 37,000 tons a year, the mines of Alsace were able to send to France no less than 47,000 tons of pure potash in the year 1919, and 30,000 tons in the first half of the present year. Many orders which were given some time ago have not yet been delivered, but the Minister of Agriculture has been able to arrange that a sufficient number of trains shall be placed at the disposal of the mines, to ensure the delivery of 5000 to 8000 tons of pure potash a month. It is therefore to be presumed that delays in delivery will no longer occur.

A WORLD'S MARKET IN PARIS.—The Federation of British Industries has undertaken the direct representation for Great Britain and the

Dominions of the Paris "Marche du Monde." The idea of establishing a "World's Market" in Paris was conceived in 1919, and from the first received the close attention and approval of the Federation. After a year's work the scheme has now come very close to practical realisation. The site for the building is being cleared, and contracts for its erection have been placed. Already a very considerable number of American, French, Italian, and other Continental, as well as some British firms have reserved space in the "Marche du Monde" when completed. At this stage the Federation of British Industries has decided in the interests of the British manufacturer to give active support to the scheme. It is most important that the Industry of this country should be fully represented at this great gathering place of trade. It is with the object of assuring that an adequate share of space should be allotted to British firms in the "Marche du Monde" and that their interests should be properly protected that the F.B.I. has decided to take over its representation here and in the Dominions overseas. The Federation recommends manufacturers engaged in or contemplating export trade to give the following brief outline of the "Marche du Monde" their earnest consideration. Briefly, the idea of the promoters is to systematise and centralise international commerce by erecting in Paris—which geographically and historically is the focus of Europe—a great commercial centre, in which the manufactures of all nations can be permanently exhibited under one roof and therefore readily accessible to buyers from all countries visiting Paris. In effect, it is a development of the City Trade Fair for which France is famous. But whereas the City Fair is temporary and local, the "Marche du Monde" will be permanent and international. Both buyer and seller will benefit, and it is for this reason that the appeal made by the "Marche du Monde" to both buyer and seller will be readily appreciated. It will enable the prospective buyer to find the firms and goods he wishes to see congregated under one roof; to make his choice from the products of many countries, with a fraction of the time, energy, and expense entailed in visiting isolated firms scattered through a multitude of towns in a dozen different countries. Conversely, it will enable the manufacturer not only to reach many more buyers, but to get into direct touch with them, and at the same time to cut expenses by obviating the necessity for so many agents or so much advertisement. It will be possible for a foreign firm to maintain a Paris or Continental Branch at a mere fraction of the cost which would otherwise have to be incurred. An Office in the building may be taken for as little—taking a favourable exchange into consideration—as £100 per year. Although it is difficult to say what the total expenditure will be, an opinion is expressed that the expenses of an office in the "Marche du Monde" looked after by a whole-time clerk who would be under the supervision of the firm's agent, will not cost more than £300 a year. It is hoped that these facts will induce manufacturers in this country to consider the matter very carefully. Any further information desired may be obtained immediately on application to the "Marche du Monde," Exhibition Section of the Federation of British Industries, 39, St. James's Street, London, S.W.1.

NOTICES.

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ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

By C. T. HEYCOCK, M.A., F.R.S.,
President of the Section.

DURING its past eighty-nine years of useful life, the British Association has, in the course of its evolution, established certain traditions; among these is the expectation that the sectional President shall deliver an address containing a summary of that branch of natural knowledge with which he has become especially acquainted.

The rapid accumulation of experimental observations during the last century, and the consequent necessity for classifying the observed facts with the aid of hypotheses and theories of ever-increasing complexity, make such summaries of knowledge essential, not only to the student of science, but also to the person of non-specialised education who desires to realise something of the tendencies and of the results of modern science.

At the present moment, when the whole world is in pause after having overcome the greatest peril which has ever threatened civilisation; when all productive effort, social, artistic, and scientific, is undergoing reorganisation preparatory to an advance which will eclipse in importance the progress made during the nineteenth century, such attempts to visualise the present condition of knowledge as are made in our Presidential Addresses are of particular value. It is, therefore, hardly necessary for me to apologise for an endeavour to place before you a statement upon the particular branch of science to which I have myself paid special attention; whatever faults may attend the mode of presentation, such a survey of a specific field of knowledge cannot but be of value to some amongst us.

I propose to deal to-day with the manner in which our present rather detailed knowledge of metallic alloys has been acquired, starting from the sparse information which was available thirty or forty years ago; to show the pitfalls which have been avoided in the theoretical interpretation of the observed facts, and to sketch very briefly the present position of our knowledge.

The production of metals and their alloys undoubtedly constitutes the oldest of those chemical arts which ultimately expanded into the modern science of chemistry, with all its overwhelming mass of experimental detail and its intricate interweaving of theoretical interpretation of the observed facts. Tubal-Cain lived during the lifetime of our common ancestor, and was "an instructor of every artificer in brass and iron"; and although it may be doubted whether the philologists have yet satisfactorily determined whether Tubal-Cain was really acquainted with the manufacture of such a complex metallic alloy as brass, it is certain that chemical science had its beginnings in the reduction of metals from their ores and in the preparation of useful alloys from those metals. In fact, metallic alloys, or mixtures of metals, have been used by mankind for the manufacture

of implements of war and of agriculture, of coinage, statuary, cooking vessels, and the like from the very earliest times.

In the course of past ages an immense amount of practical information has been accumulated concerning methods of reducing metals, or mixtures of metals, from their ores, and by subsequent treatment, usually by heating and cooling, of adapting the resulting metallic product to the purpose for which it was required. Until quite recent times, however, the whole of this knowledge was entirely empirical in character, because it had no foundation in general theoretical principles; it was collected in haphazard fashion in accordance with that method of trial and error which led our forerunners surely, but with excessive expenditure of time and effort, to valuable results.

To-day I purpose dealing chiefly with the non-ferrous alloys, not because any essential difference in type exists between the ferrous and non-ferrous alloys, but merely because the whole field presented by the chemistry of the metals and their alloys is too vast to be covered in any reasonable length of time.

The earliest recorded scientific investigations on alloys were made in 1722 by Reaumur, who employed the microscope to examine the fractured surfaces of white and grey cast iron and steel.

In 1808 Widmanstätten cut sections from meteorites, which he polished and etched.

The founder, however, of modern metallography is undoubtedly H. C. Sorby, of Sheffield. Sorby's early petrographic work on the examination of thin sections of rock under the microscope led him to a study of meteorites and of iron and steel, and in a paper read before the British Association in 1864 he describes briefly (I quote his own words) how sections "of iron and steel may be prepared for the microscope so as to exhibit their structure to a perfection that leaves little to be desired. They show various mixtures of iron, and two or three well-defined compounds of iron and carbon, graphite, and slag; these constituents being present in different proportions and arranged in various manners, give rise to a large number of varieties of iron and steel, differing by well-marked and very striking peculiarities of structure." The methods described by Sorby for polishing and etching alloys and his method of vertical illumination (afterwards improved by Beck) are employed to-day by all who work at this branch of metallography.

The lantern-slides, now shown, were reproduced from his original photographs; they form a lasting memorial to his skill as an investigator and his ability as a manipulator. In 1887, Dr. Sorby published a paper on the microscopical structure of iron and steel in the *Journal of the Iron and Steel Institute*. This masterpiece of clear writing and expression, even with our present knowledge, needs but little emendation. In this paper he describes Free Iron (ferrite) carbon as graphite, the pearly constituent as a very fine laminar structure (pearlitic structure), combined iron as the chief constituent of white cast iron (cementite), slag inclusions, effect of tempering steel, effect of working iron and steel, cementation of wrought iron, and the decarbonisation of cast iron by haematite. A truly remarkable achievement for one man.

From 1854-68, Mattheisen published in the Reports of the British Association and in the Proceedings and Transactions of the Royal Society, a large number of papers on the electrical conductivity, tenacity, and specific gravity of pure metals and alloys. He concluded that alloys are either mixtures of definite chemical compounds with an excess of one or other metal, or solutions of the definite alloy in the excess of one of the metals employed, forming, in their solid condition, what he called a solidified solution. This idea of a solidified solution has developed into a most fruitful theory upon which much of our modern notions of alloys depends. Although, at the time, the experiments on the electrical conductivity did not lead to very definite conclusions, the method has since been used with great success in testing for the presence of minute quantities of impurities in the copper used for conductors.

In the *Philosophical Magazine* for 1875, F. Guthrie, in a remarkable paper, quite unconnected with alloys, gave an account of his experiments on salt solutions and attached water. He was led to undertake this work by a consideration of a paper by Dr. J. Rea, the Arctic explorer, on the comparative saltiness of freshly formed and of older ice floes. Guthrie showed that the freezing-point of solutions was continuously diminished as the percentage of common salt increased, and that this lowering increased up to 23.6 per cent of salt, when the solution solidified as a whole at about 22° C. He further showed, and this is of great importance, that the substance which first separated from solutions more dilute than 23.6 was pure ice. To the substance which froze as a whole, giving crystals of the same composition as the mother liquor, he gave the name cryohydrate. At the time he thought that the cryohydrate of salt containing 23.6 per cent NaCl and 76.4 per cent of water was a chemical compound $2\text{NaCl} \cdot 21\text{H}_2\text{O}$. In succeeding years he showed that a large number of other salts gave solutions which behaved in a similar manner to common salt. He abandoned the idea that the cryohydrates were chemical compounds.

How clear his views were will be seen by quotations from his paper in the *Phil. Mag.* (5) I. and II., 1876, in which he states: (i.) When a solution weaker than the cryohydrate loses heat, ice is formed. (ii.) Ice continues to form and the temperature to fall until the cryohydrate is reached. (iii.) At the point of saturation ice and salt separate simultaneously and the solid and liquid portions are identical in composition.

These results can be expressed in the form of a simple diagram as shown in the slide.

In a subsequent paper, *Phil. Mag.* (5) 17, he extends his experiments to solvents other than water, and states that the substances which separate at the lowest temperature are neither atomic nor molecular; this lowest melting-point mixture of two bodies he names the eutectic mixture. In the same paper, he details the methods of obtaining various eutectic alloys of bismuth, lead, tin, and cadmium.

We have, in these papers of Guthrie's, the first important clue to what occurs on cooling a fused mixture of metals. The researches of Sorby and Guthrie, undertaken as they were for the sake of investigating natural phenomena, are a remarkable example of how purely scientific experiment

can lead to most important practical results. It is not too much to claim for these investigators the honour of being the originators of all our modern ideas of metallurgy. Although much valuable information had been accumulated, no rapid advance could be made until some general theory of solution had been developed. In 1878 Raoult first began his work on the depression of the freezing-point of solvents due to the addition of dissolved substances, and he continued, at frequent intervals, to publish the results of his experiments up to the time of his death in 1901. He established for organic solvents certain general laws: (i.) that for moderate concentrations the fall of the freezing-point is proportional to the weight of the dissolved substance present in a constant weight of solvent; (ii.) that when the falls produced in the same solvent by different dissolved substances are compared, it is found that a molecular weight of a dissolved substance produces the same fall of the freezing-point, whatever the substance is. When, however, he applied the general laws which he had established for organic solvents to aqueous solutions of inorganic acids, bases, and salts, the results obtained were hopelessly discrepant. In a paper in the *Zeit. Physik. Chem.* for 1888 on "Osmotic Pressure in the analogy between solutions and gases," Van't Hoff showed that the experiments of Pfeffer on osmotic pressure could be explained on the theory that dissolved substances were, at any rate for dilute solutions, in a condition similar to that of a gas; that they obeyed the laws of Boyle, Charles, and Avogadro, and that on this assumption the depression of the freezing-point of a solvent could be calculated by means of a simple formula. He also showed that the exceptions which occurred to Raoult's laws, when applied to aqueous solutions of electrolytes, could be explained by the assumption, first made by Arrhenius, that these latter in solution are partly dissociated into their ions. The result of all this work was to establish a general theory applicable to all solutions which has been widespread in its applications. It is true that Van't Hoff's theory has been violently attacked; but it enables us to calculate the depression of the freezing-points of a large number of solvents. To do this it is necessary to know the latent heat of fusion of the pure solvent and the absolute temperature of the freezing-point of the solution. That the numbers calculated are in very close accord with the experimental values constitutes a strong argument in favour of the theory. From this time the study of alloys began to make rapid progress. Laurie (*Chem. Soc. Jour.*, 1888), by measuring the potential difference of voltaic cells composed of plates of alloy and the more negative element immersed in a solution of a salt of one of the component metals, obtained evidence of the existence of compounds such as $\text{CuZn}_2\text{Cu}_3\text{Sn}$. In 1889, F. H. Neville and I, whilst repeating Raoult's experiments on the lowering of the freezing-point of organic solvents, thought that it was possible that the well-known fact that alloys often freeze at a lower temperature than either of their constituents might well be explained in a similar way. In a preliminary note communicated to the Chemical Society on March 21, 1889, on the same evening that Professor Ramsay read his paper on the molecular weights of metals as determined

Table of Freezing-points.

	Carnelly's Tables.	Holborn & Wien 1892	Callendar & Griffiths. 1892	Neville & Heycock, 1895	Burgess & Le Chatelier, 1912. High Tem- perature Measurements.
Tin	—	—	231·7	231·9	231·9
Zinc	433	—	417·6	419·0	419·4
Lead	—	—	—	327·6	327·4
Antimony	432	—	—	629·5	630·7 & 629·2
Magnesium	—	—	—	632·6	650·0
Aluminium	700.	—	—	654·5	658·0
Silver	954	968	972·0	960·7	960·9
Gold	1045	1072	1037·0	1061·7	1062·4
Copper	1054	1082	—	1080·5	1083·0
Sulphur B.P.	448	—	444·53	—	444·7

¹ Contaminated with silicon.

² Known to be impure.

by the depression of the vapour pressure, we showed that the fall produced in the freezing-point of tin by dissolving metals in it was for dilute solutions directly proportional to the concentration. We also showed that the fall produced in the freezing-point of tin by the solution of one atomic weight of metal in 100 atomic weights of tin was a constant.

G. Tannman about the same time (*Zeit. Physik. Chemie*, 1889, iii., 44) arrived at a similar conclusion, using mercury as a solvent.

These experiments helped to establish the similarity between the behaviour of metallic solutions or alloys and that of aqueous and other solutions of organic compounds in organic solvents. That our experiments were correct seemed probable from the agreement between the observed depression of the freezing-point and the value calculated from Van't Hoff's formula for the case of those few metals whose latent heats of fusion had been determined with any approach to accuracy.

Our experiments, subsequently extended to other solvents, led to the conclusion that in the case of most metals dissolved in tin the molecular weight is identical with the atomic weight; in other words, that the metals in solution are monatomic. This conclusion, however, involves certain assumptions. Prof. Ramsay's experiments on the lowering of the vapour pressure of certain amalgams point to a similar conclusion.

So far our work had been carried out with mercury thermometers, standardised against a platinum resistance pyrometer, but it was evident that, if it was to be continued, we must have some method of extending our experiments to alloys which freeze at high temperatures. The thermo couple was not at this stage a reliable instrument; fortunately, however, Callendar and Griffiths had brought to great perfection the electrical resistance pyrometer (*Phil. Trans.*, A, 1887 and 1891). Dr. E. H. Griffiths kindly came to our aid, and with his help we installed a complete electrical resistance set. As at this time the freezing-points of pure substances above 300° were not known with any degree of accuracy, we began by making the measurements shown in Table.

With the exception of silver and gold, these metals were the purest obtainable in commerce.

Two facts are evident from the consideration of this table: (a) the remarkable accuracy of Callendar's formula connecting the Temperature Centigrade with the change of resistance of a pure platinum wire; (b) the accuracy of Callendar and Griffiths' determination of the boiling-point of

sulphur. Although the platinum resistance pyrometer had at this time only been compared with the air thermometer up to 600° C., it will be noted that the extrapolation from 600° to nearly 1100 was justified.

I cannot leave the subject of high-temperature measurements without referring to the specially valuable work of Burgess, and also to Eza Griffiths' book on high-temperature measurements which contains an excellent summary of the present state of our knowledge of this important subject.

During the period that the above work on non-ferrous alloys was being done, great progress was being made in the study of iron and steel by Osmond and Le Chatelier. In 1890 the Institute of Mechanical Engineers, not apparently without considerable misgivings on the part of some of its members, formed an Alloys Research Committee. This Committee invited Professor (afterwards Sir William) Roberts-Austen to undertake research work for them. The results of his investigations are contained in a series of five valuable Reports extending from 1891 to 1899, published in the Journal of the Institute. The first report contained a description of an improved form of Le Chatelier recording pyrometer, and the instrument has since proved a powerful weapon of research. In the second report, issued in 1893, the effects on the properties of copper of small quantities of arsenic, bismuth, and antimony were discussed. Whilst some engineers advocated, others as strongly controverted, the beneficial results of small quantities of arsenic on the copper used for the fireboxes of locomotives. The report showed that the presence of from 0·5-1 per cent of arsenic was highly beneficial. The third report dealt with electric welding and the production of alloys of iron and aluminium. The fourth report is particularly valuable, as it contains a *résumé* of the Bakerian Lecture given by Roberts-Austen on the diffusion of metals in the solid state, in which he showed that gold, even at as low a temperature as 100°, could penetrate into lead, and that iron became carbonised at a low red heat by contact with a diamond in a vacuum. In 1899 the fifth report appeared on the effects of the addition of carbon to iron. This report is of especial importance, because, besides a description of the thermal effects produced by carbon, which he carefully plotted and photographed, he described the microscopical appearance of the various constituents of iron. The materials of this report, together with the work of Osmond

and others on steel and iron, provided much of the material on which Professor Bakhuis Roozeboom founded the iron carbon equilibrium diagram. Reference should also be made to the very valuable paper by Stansfield on the present position of the solution theory of carbonised iron (*Journ. Iron and Steel Inst.*, 1900, xi., 317). It may be said of this fifth report, and the two papers just referred to, that they form the most important contribution to the study of iron and steel that has ever been published. Although the diagram for the equilibrium of iron and carbon does not represent the whole of the facts, it affords the most important clue to these alloys, and undoubtedly forms the basis of most of the modern practice of steel manufacture. (Slide showing iron carbon diagram).

Many workers, both at home and abroad, were now actively engaged in metallurgical work—Stead, Osmond, Le Chatelier, Arnold, Hadfield, Carpenter, Ewing, Rosenhain, and others too numerous to mention.

In 1897, Neville and I determined the complete freezing-point curve of the copper-tin alloys, confirming and extending the work of Roberts-Austen, Stansfield, and Le Chatelier; but the real meaning of the curve remained as much a mystery as ever. Early in 1900, Sir G. Stokes suggested to us that we should make a microscopic examination of a few bronzes as an aid to the interpretation of the singularities of the freezing-point curve. An account of this work, which occupied us for more than two years, was published as the Bakerian Lecture of the Royal Society in February, 1903. Whilst preparing a number of copper-tin alloys of known composition we were struck by the fact that the crystalline pattern which developed on the free surface of the slowly cooled alloys was entirely unlike the structure developed by polishing and etching sections cut from the interior; it therefore appeared probable that changes were going on within the alloys as they cooled. In the hope that, as Sorby had shown in the case of steel, we could stereotype or fix the change by sudden cooling, we melted small ingots of the copper-tin alloys and slowly cooled them to selected temperatures and then suddenly chilled them in water. The results of this treatment were communicated to the Royal Society and published in the *Proceedings*, February, 1901. (Slides showing effects of chilling alloys).

To apply this method to a selected alloy we first determined its cooling curve by means of an automatic recorder, the curve usually showing several halts or steps in it. The temperature of the highest of these steps corresponded with a point on the liquidus, *i.e.*, when solid first separated out from the molten mass. To ascertain what occurred at the subsequent halts, ingots of the melted alloy were slowly cooled to within a few degrees above and below the halt and then chilled, with the result just seen on the screen.

The method of chilling also enabled us to fix, with some degree of accuracy, the position of points on the solidus. If an alloy, chilled when it is partly solid and partly liquid, is polished and etched, it will be seen to consist of large primary combs embedded in a matrix consisting of mother liquor, in which are disseminated numerous small combs, which we called "chilled primary." By repeating the process at successively lower and

lower temperatures we obtained a point at which the chilled primary no longer formed, *i.e.*, the upper limit of the solidus.

Although we made but few determinations of the physical properties of the alloys, it is needless to say how much they vary with the temperature and with the rapidity with which they are heated or cooled.

From a consideration of the singularities in the liquidus curve, coupled with the microscopic examination of slowly cooled and chilled alloys, we were able to divide the copper-tin alloys into certain groups having special qualities. It would take far too long to discuss these divisions. In interpreting our result we were greatly assisted not only by the application of the phase rule, but also by the application of Roozeboom's theory of solid solution (unfortunately Professor Roozeboom's letters were destroyed by fire in June, 1910) and by the advice he kindly gave us. At the time the paper was published we expressly stated that we did not regard all our results as final, as much more work was required to clear up points still obscure. Other workers—Shepherd and Blough, Giolitti and Tavanti—have somewhat modified the diagram. (Slides shown).

Neither Shepherd and Blough nor Hoyt have published the photomicrographs upon which their results are based, so that it is impossible to criticise their conclusions. Giolitti and Tavanti have published some microphotographs, from which it seems that they had not allowed sufficient time for equilibrium to be established. In this connection I must call attention to the excellent work of Haughton on the constitution of the alloys of copper and tin (*Journ. Institute of Metals*, March, 1915). He investigated the alloys rich in tin, and illustrated his conclusions by singularly beautiful microphotographs, and has done much to clear up doubtful points in this region of the diagram. I have dwelt at some length on this work, for copper-tin is probably the first of the binary alloys on which an attempt has been made to determine the changes which take place in passing from one pure constituent to the other. I would again call attention to the fact that without a working theory of solution the interpretation of the results would have been impossible.

Since 1900, many complete equilibrium diagrams have been published; amongst them may be mentioned the work of Rosenhain and Tucker on the lead-tin alloys (*Phil. Trans.*, 1908), in which they describe hitherto unsuspected changes on the lead rich side which go on when these alloys are at quite low temperatures, also the constitution of the alloys of aluminium and zinc; the work of Rosenhain and Archbutt (*Phil. Trans.*, 1911), and quite recently the excellent work of Vivian, on the alloys of tin and phosphorus, which has thrown an entirely new light on this difficult subject.

So far I have called attention to some of the difficulties encountered in the examination of binary alloys. When we come to ternary alloys, the difficulties of carrying out an investigation are enormously increased, whilst with quaternary alloys they seem almost insurmountable; in the case of steels containing always six, and usually more, constituents, we can only hope to get information by purely empirical methods.

Large numbers of the elements and their compounds which originally were laboriously prepared and investigated in the laboratory and remained dormant as chemical curiosities for many years have, in the fulness of time, taken their places as important and, indeed, essential articles of commerce. Passing over the difficulties encountered by Davy in the preparation of metallic sodium and by Faraday in the production of benzene (both of which materials are manufactured in enormous quantities at the present time), I may remark that even during my own lifetime I have seen a vast number of substances transferred from the category of rare laboratory products to that which comprises materials of the utmost importance to the modern metallurgical industries. A few decades ago, aluminium, chromium, cerium, thorium, tungsten, manganese, magnesium, molybdenum, nickel, calcium and calcium carbide, carborundum, and acetylene, were unknown outside the chemical laboratory of the purely scientific investigator; to-day these elements, their compounds and alloys, are amongst the most valuable of our industrial metallic products. They are essential in the manufacture of high-speed steels, of armour plate, of filaments for the electric bulb lamp, of incandescent gas mantles, and of countless other products of modern scientific industry.

All these metallic elements and compounds were discovered, and their industrial uses foreshadowed, during the course of the purely academic research work carried out in our Universities and Colleges; all have become the materials upon which great and lucrative industries have been built up. Although the scientific worker has certainly not exhibited any cupidity in the past—although he has been content to rejoice in his own contributions to knowledge, and to see great manufacturing enterprises founded upon his work—it is clear that the obligation devolves upon those who have reaped in the world's markets the fruit of scientific discovery to provide from their harvest the financial aid without which scientific research cannot be continued.

The truth of this statement is well understood by those of our great industrial leaders who are engaged in translating the results of scientific research into technical practice. As evidence of this I may quote the magnificent donation of £210,000 by the British Oil Companies towards the endowment of the School of Chemistry in the University of Cambridge, the noble bequest of the late Dr. Messel, one of the most enlightened of our technical chemists, for defraying the cost of scientific research, the gifts of the late Dr. Ludwig Mond towards the upkeep and expansion of the Royal Institution, one of the strongholds of British chemical research, and the financial support given by the Goldsmiths' and others of the great City of London Livery Companies (initiated largely by the late Sir Frederick Abel, Sir Frederick Bramwell, and Mr. George Matthey), to the foundation of the Imperial College of Science and Technology. The men who initiated these gifts have been themselves intimately associated with developments both in science and industry; they have understood that the field must be prepared before the crop can be reaped. Fortunately, our great chemical industries are, for the most part, controlled and administered by men fully conversant with the mode in which technical progress and prosperity follow

upon scientific achievement; and it is my pleasant duty to record that within the last few weeks the directors of one of our greatest chemical-manufacturing concerns have, with the consent of their shareholders, devoted £100,000 to research. Doubtless other chemical industries will in due course realise what they have to gain by an adequate appreciation of pure science.

If the effort now being made to establish a comprehensive scheme for the resuscitation of chemical industry within our Empire is to succeed, financial support on a very liberal scale must be forthcoming from the industry itself, for the advancement of purely scientific research. This question has been treated recently in so able a fashion by Lord Moulton that nothing now remains but to await the results of his appeal for funds in aid of the advancement of pure science.

In order to prevent disappointment, and a possible reaction in the future, in those who endow pure research, it is necessary to give a word of warning. It must be remembered that the history of science abounds in illustrations of discoveries, regarded at the time as trivial, which have in after years become epoch-making.

In illustration, I would cite Faraday's discovery of electro-magnetic induction. He found that when a bar magnet was thrust into the core of a bobbin of insulated copper wire, whose terminals were connected with a galvanometer, a momentary current was produced; whilst on withdrawing the magnet a momentary reverse current occurred; a purely scientific experiment destined in later years to develop into the dynamo and with it the whole electrical industry. Another illustration may be given: Guyton de Morveau, Northmore, Davy, Faraday, and Cagniard Latour between 1800 and 1850 were engaged in liquefying many of the gases. Hydrogen, oxygen, nitrogen, marsh gas, carbon-monoxide, and nitric oxide, however, resisted all efforts, until the work of Joule and Andrews gave the clue to the causes of failure. Some thirty years later by careful application of the theoretical considerations all the gases were liquefied. The liquefaction of oxygen and nitrogen now forms the basis of a very large and important industry.

Such cases can be multiplied indefinitely in all branches of science.

Perhaps the most pressing need of the present day lies in the cultivation of a better understanding between our great masters of productive industry, the shareholders to whom they are in the first degree responsible, and our scientific workers; if, by reason of any turbidity of vision, our large manufacturing corporations fail to discern that, in their own interest, the financial support of purely scientific research should be one of their first cares, technical advance will slacken and other nations, adopting a more far-sighted policy, will forge ahead in science and technology. It should, I venture to think, be the bounden duty of everyone who has at heart the aims and objects of the British Association to preach the doctrine that in closer sympathy between all classes of productive labour, manual and intellectual, lies our only hope for the future. I cannot do better than conclude by quoting the words of Pope, one of our most characteristically British poets: "By mutual confidence and mutual aid Great deeds are done and great discoveries made."

A MODIFIED THEORY
OF THE CROOKES RADIOMETER.

By GILBERT D. WEST, D.Sc. (Lond.)

A STRIKING feature of the physical literature of the period 1874-1881 is the extraordinary amount of interest that was raised by Crookes' researches "On the Repulsion Resulting from Radiation." In addition to Crookes himself, Fitzgerald, Johnstone-Stoney, Stokes, Schuster, Pringsheim, Osborne-Reynolds, and Maxwell, all gave the phenomena their attention. It was the work of Osborne-Reynolds and Maxwell, however, that was held to settle the numerous discussions that had arisen. These physicists showed in two long and highly mathematical Papers, published in the *Phil. Trans.* of 1879, that the phenomena under notice were explicable in terms of the then somewhat new kinetic theory of gases. As a result of their Papers, the interest in the theory of the radiometer—great though it had previously been—subsided, and but for a criticism of Reynolds' work from Fitzgerald in 1881 (*Phil. Mag.*, 1881, xi., 103), there is little worth recording for the next sixteen years. It would seem that this change occurred, largely because the majority of physicists felt that the matter had been placed beyond their grasp, rather than because some well-understood explanation had been given which rendered further research superfluous. According to Fitzgerald, Reynolds had rendered "a difficult subject tenfold as elaborate as was necessary," but however this may be, it is certain that an easily intelligible explanation of radiometric phenomena was wanted. Attempts were made, it is true, to give the substance of the accepted theories in general language but, although many of the text book "explanations" are still based on these, it cannot be said that they met with much success.

In 1896, however, Sutherland turned his attention to the subject, and his Paper (*Phil. Mag.*, 1896, xlii., 373 and 476) had the advantage that, unlike those of Reynolds and Maxwell, it could be read with profit by the physicist of ordinary mathematical attainments. Yet appearing at it did at a time when the interest in the theory of the radiometer had practically ceased, it was neglected, and has since become almost entirely forgotten.

It was shown by the author (*Proc. Phys. Soc.*, 1919, xxxi., 278), however, that Sutherland's theory of the closely related phenomena of thermal transpiration was so far correct, that it could be made to form an adequate basis for the careful experimental work of the Danish physicist, Knudsen, performed thirteen years later. The author was thus tempted to place considerable confidence in Sutherland's theory of the radiometer. It must be observed, however, that, at the time when Sutherland wrote his paper, little was known of the thermal surface conditions in a rarefied gas, and thus it is not surprising to find that Sutherland's theory—like many another imperfect theory in other branches of physics—will explain some of, but not all the experimental facts. It is the object of the present Paper to outline a theory of a general descriptive character which, while being to a large extent based on Sutherland's work, makes use of knowledge gained since that time.

Sutherland, like Reynolds, bases his theory of the radiometer on the closely related phenomena of thermal transpiration. He first considers the case of a tube along which a temperature gradient is maintained. If the tube connects two infinite spaces, he shows that an even flow of gas takes place over the whole cross section of the tube from the hot to the cold side. The walls of the tube in thus constraining the gas to take their temperature, exert a tangential traction upon it, whilst they themselves experience a reaction in the opposite direction. A nett reaction is only experienced however, near the entrance of the tube, where the velocity of the gas rises from zero to the uniform value eventually attained. At all other parts of the tube the friction of the moving gas against the walls of the tube exactly balances the traction the walls exert on the gas; it is to the "unequilibrated traction," however, that Sutherland attaches most importance.

If the spaces the tube connects are finite, the uniform flow of gas produces a pressure in the hot vessel, which in turn produces a flow of the Poiseuille type in the reverse direction to the original flow. The result of the superposition of these two flows is to give a gas current from the cold to the hot side along the walls of the tube, together with a current from the hot to the cold side along the axis, whilst between the two currents there is a surface of zero velocity.

With reduction of gas pressure, the Poiseuille counter flow becomes less and less important, until at the highest rarefactions it is negligible, and the hot regions are then enabled to maintain undiminished their higher pressures.

Sutherland points out that both the "unequilibrated traction" and the thermal transpiration pressure operate in causing radiometer motion, and to make his meaning clear he takes the case of a piston that fits loosely into a cylinder closed at both ends. He imagines the temperature of one compartment to be higher than that of the other, and that a temperature gradient exists in the material of the piston. As a consequence of the operation of thermal transpiration, the pressure on the hot side will become greater than that on the cold side, and a force will be exerted on the piston, both as a result of this excess pressure in the hot compartment, and as a result of the unequilibrated traction on the sides of the piston. By increasing the clearance between the piston and the cylinder, the thermal transpiration pressure can be made to bear an ever-decreasing ratio to the total thrust on the piston. If the piston be free to move, it constitutes, according to Sutherland, an exaggerated example of radiometer motion, and he formulates his theory on these lines.

It must be admitted, however, that to pass from the case of the piston to that of the vane of a Crookes radiometer, is a big step. Nevertheless, Sutherland maintains that such a step is legitimate and proceeds, with considerable success, to analyse the experimental data obtained with a type of torsion radiometer. Except in so far as it was better suited to give quantitative measurements, this type did not differ materially from the familiar type in which flat circular vanes, blackened on one side and silvered on the other, are mounted at the ends of a pivoted arm. "When the black face is irradiated," he says, "there is a fall of

temperature . . . through the thickness of the vane, and thus the thickness of the vane becomes a surface capable, along with the surface of the bulb opposite it, of starting thermal transpiration from the cold edge to the hot, with elevation of pressure in front of the hot face . . . and depression of that behind the cold face."

Such, briefly, is an outline of Sutherland's theory, but it is clear, as indeed he himself states, that it is based on the idea that the effect of the introduction of a heated body into a gas is "to make the layer of gas in contact with the solid take the temperature of the solid at every point of the surface." It has since been realised, of course, that this is not so, and that in any calculation made in regard to rarefied gases due allowance must be made for the temperature discontinuity at the surface of the solid.

To make what is meant more clear, consider the case of two large parallel plates—one hot and the other cold. We may regard the molecules that strike the hot surface, both as coming from a distance of the order of the mean free path, and as possessing the temperature of this region. If, after reflection at the surface, these molecules merely acquire its temperature, it is clear that the mean temperature of the surface layer of gas is necessarily lower than that of the surface itself. As a matter of fact, however, it has been shown (Soddy and Berry, *Proc. Royal Soc., A*, 1911, lxxxiv., 576; Knudsen, *Ann. d. Phys.*, 1911 xxxiv., 4, p. 593; Smoluchowski, *Phil. Mag.*, 1911, xxi., 11; Langmuir, *Phys. Rev.*, 1913, ii., No. 5, p. 329) that, on the average impinging molecules do not even acquire the temperature of the surface they strike, and hence the discontinuity already noted becomes enhanced.

Thus in the light of modern research, one of Sutherland's assumptions is seen to be unjustifiable, and the theory built upon it must therefore be imperfect. It is possible, however, to modify the theory.

Consider once again the case of the hot and cold plates, but now with reference to the change that takes place in the isothermals, as the pressure is lowered. It is clear that, with increasing mean free path, the extreme isothermals will disappear, and that eventually, when the mean free path becomes large compared to the distance apart of the plates, the gas between will reach a uniform mean temperature. Reduction of gas pressure will thus be accompanied by a gradual diminution, and eventual elimination, of the temperature gradient between the plates.

In the particular case considered it is easy to calculate the positions of the isotherms with changing gas pressure, but in the case of a radiometer vane this is much more difficult. However, the present purpose is served quite well if a general indication is given of the changes that take place.

To make matters simple, consider first of all the case of a disc with the hot surface A 10° C. above the cold surface B—the walls of the containing vessel being supposed distant, and at the mean of the temperatures of the hot and cold surfaces. In Fig. 1 the isotherms in the gas are drawn for the case where the gas pressure is very high, whilst in Fig. 2 a rough idea is given of their appearance at a lower pressure. It will be

seen that the extreme isothermals have disappeared, and that, so far as the gas is concerned, neither surface of the disc coincides with an isothermal surface. On the contrary, a temperature gradient extends from the circumference towards the centre.

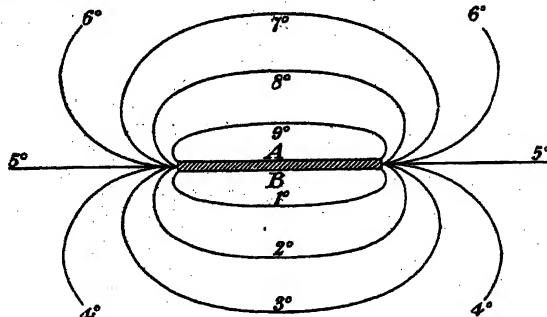


FIG. 1.—ISOTHERMS AROUND RADIOMETER VANE—PRESSURE HIGH.

Such a temperature gradient in the surface layer of gas was encountered in the experiments described in a previous paper by the author on the forces acting on heated metal foil surfaces in rarefied gases (*Proc. Phys. Soc.*, 1920, xxxii.), and it was there shown that satisfactory explanations

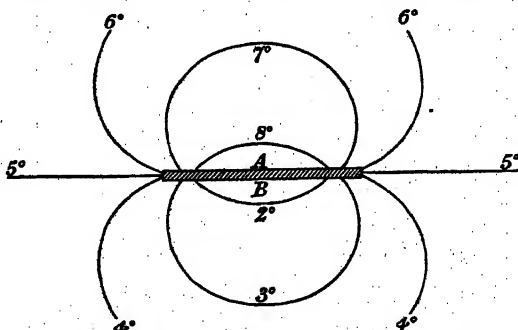


FIG. 2.—ISOTHERMS AROUND RADIOMETER VANE—PRESSURE LOW.

could be based on the assumption that this temperature gradient gave rise to gas currents somewhat similar to those arising in a tube in the material of which a temperature gradient was maintained in the direction of the length.

If, as would appear legitimate, we can apply similar reasoning to a radiometer vane we shall have to imagine a flow of gas to take place similar to that indicated in Fig. 3. On the cold side B, the gas will be flowing outwards from the centre, with consequent reduction of pressure on the vane, whilst on the hot side A it will be

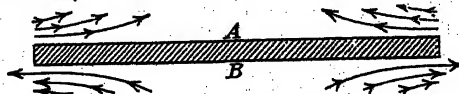


FIG. 3.—FLOW AROUND RADIOMETER VANE.
A is Hot Surface, B is Cold Surface.

flowing inwards towards the centre, with consequent increase of pressure on the vane. When the gas pressure is fairly high, and when the

isotherms have consequently not departed much from the shapes indicated in Fig. 1, the flow of gas and the regions of excess and defect of pressure will be restricted to the peripheral portions of the disc. When, however, the gas pressure is

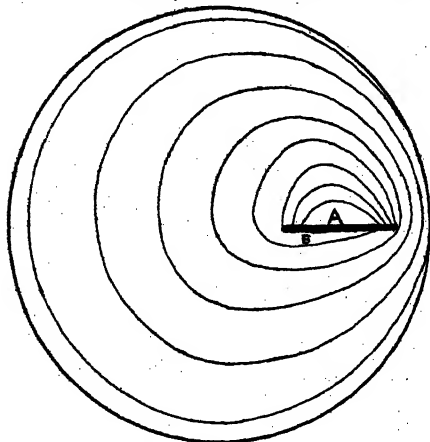


FIG. 4.—ISOTHERMS AROUND RADIOMETER VANE IN SPHERICAL GLASS BULB—MEDIUM GAS PRESSURE.*

A is Hot Surface, B is Cold Surface.

lowered, the area over which the excess or defect of pressure is felt, will extend towards the centre, until at last the whole surface of the disc will be covered.

The shapes of the isotherms surrounding an actual radiometer vane enclosed in a spherical bulb are, of course, again far too complicated to calculate. From general considerations, however, it is possible to give a rough idea of their shapes. In practice, one side of the vane, although much cooler than the other, is still slightly above the temperature of the glass walls, and under such conditions Fig. 4 might represent sufficiently well the forms the isotherms would take at a medium gas pressure. An indication is also given in Fig. 5 of the directions in which the

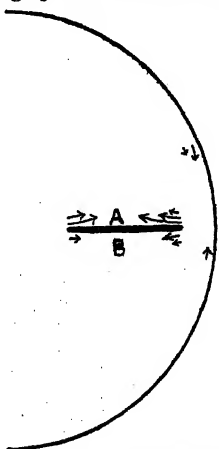


FIG. 5.—FLOW AROUND RADIOMETER VANE IN SPHERICAL GLASS BULB.

A is Hot Surface, B is Cold Surface.

gas currents would flow. It will be seen that on both sides of the vane they flow towards the central region, but that on the hot side the flow is much more vigorous owing to the greater temperature gradient. It will be noticed further that the flow is greatest on the edge of the disc nearest the glass, and also that in the gas layer on the glass itself there are two regions each capable of producing excess pressures—the most effective region being near the hot side of the disc.

Briefly, therefore, the modification introduced by the present explanation consists chiefly in a difference in the temperature ascribed to the surface layer of gas covering the vane, and in a consequent difference in the regions over which the flow of gas is supposed to take place. The question naturally arises, therefore as to whether there are any radiometric phenomena that support the present view. For a reply we must turn our attention to the Crookes radiometer with slanting vanes.

In this instrument, a plan of which is shown in Fig. 6, a number of vanes are placed at an angle to the supporting radial arms. In one instrument the vanes were made of aluminium foil bright on both sides, and when radiation was allowed to fall upon them, vigorous rotation ensued (indicated in Fig. 6 by the arrow), and that in spite of an almost negligible difference in temperature of the two sides of the vanes. Crookes points out (*Phil. Trans.*, 1878, clxix, 282) that had the vanes pointed radially there would have been practically no tendency to rotation.

On Sutherland's theory, no very obvious explanation of this phenomenon can be given, but on the present theory this is at once possible.

The surfaces of the vanes will be covered on both sides by a gas layer whose temperature will rise from the edge towards the central regions.

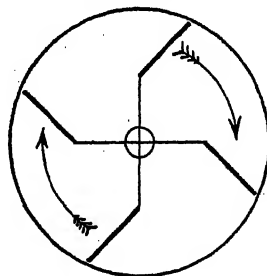


FIG. 6.—CROOKES RADIOMETER WITH SLANTING VANES.

The gradient will be steepest on the part of the disc nearest the bulb, and here also the flow of gas will be most vigorous. We have to remember, however, that the gas currents can only flow as a result of a tangential reaction exerted on the material of the vane. Hence on both its surfaces we shall have outward tangential forces, and such forces will be capable of producing rotation. The side of the vane nearest the glass, moreover, will experience a pressure resulting from the difficulty the surface currents find in escaping, but this pressure will not in general be as important as the tangential forces.

The radiometer with slanting vanes connects itself naturally with the recent experiments of

* The suggestions made by Mr. F. J. W. Whipple in the discussion embodied in this figure.

the author (*Proc. Phys. Soc.*, 1920, xxxii.) on the edgewise movements of strips of foil placed at an angle to a glass wall and exposed to the radiation from a lamp. It will be remembered that such strips showed edgewise movements towards the glass which completely masked the normal repulsion effect.

Let us now pass to the consideration of the radiometer constructed of hemispherical cups, mounted anemometer fashion. Sutherland says: "Consider a convex irradiated by a source on the normal through its middle point; then as the amount of heat that a surface absorbs depends on its obliquity to the incident radiation, the farther a part of the convex surface is from the middle, the less is it directly heated, and thus there is a continuous fall of temperature from the centre of the surface to the edge; conduction, if allowed time, tends to reduce the amount of fall but does not obliterate it, and conduction also establishes a fall of temperature along the back from the centre to the edge. Now the traction of the gas on the solid, is from hot to cold, so that both on the front and back of the vane there is a traction from centre to edge, whose resultant effect is to drag the vane away from the light when the vane is convex to it, so that the light appears to repel a convex surface. When the surface is concave the same reasoning applies, the gas exerts a traction from centre to edge, and therefore the light appears to attract it."

According to the above, therefore, the temperature gradient is made to depend on the changing obliquity of the surface of the cup. Rotation still takes place, however, when the obliquity is kept constant by replacing the hemispheres by hollow cones. It is true that, owing to a spreading of the stream lines more heat will here be conducted away from the peripheral regions of the cone than from other regions, but with cups of good conducting material, such as aluminium, the temperature gradient so produced would be very small. Previous experiments by the author have demonstrated, moreover, that such temperature gradients are not of much importance. For the rotation of the conical cups, therefore, Sutherland's theory gives no easy explanation.

If we realise, however, that a rarefied gas does not necessarily take the temperature of the surface with which it is in contact, and if we imagine, as is legitimate, that a temperature gradient, in the gas layer, extends from the periphery of the cone towards the apex, there is no difficulty in modifying Sutherland's original explanation to suit this new case. Such a modification will resemble that given for the radiometer with slanting vanes.

In his Paper, Sutherland deals with other experiments performed by Crookes, but the differences that have to be introduced into his explanations on the present theory are so small that further discussion is not necessary.

It might be said, therefore, when all the facts that have been discussed are taken into consideration, that Sutherland's theory, as it stands, is apparently not capable of explaining certain radiometric phenomena, but that when modifications, supported by modern experimental knowledge, are made in the thermal surface conditions, such explanations become at once possible.—*Proceedings of the Physical Society*, June 15, 1920.

THE ODOROUS CONSTITUENTS OF APPLES. EMANATION OF ACETALDEHYDE FROM THE RIPE FRUIT.*

By FREDERICK B. POWER and VICTOR K. CHESNUT,

THE fact that many ripe fruits possess characteristic odours is well known, but it is somewhat remarkable that so little information has been recorded respecting the chemical nature of the substances to which these odorous properties are due. This deficiency of knowledge may, however, be attributed to the extremely small proportion in which such constituents are usually present, to their more or less complex character, and to the consequent difficulties attending their separation or identification. The respective odorous substances have commonly been regarded as esters, and a number of artificially prepared compounds of this class have indeed been given names which indicate their resemblance in odour to certain fruits, such as "apple oil" for amyl valerate, "pear oil" for amyl acetate, and "pineapple oil" for ethyl butyrate. The so-called artificial fruit essences are, however, usually composed of a mixture of substances, without any consideration of their actual occurrence in the fruits whose flavours they are supposed to represent. An actual identification of the principal flavouring constituent of an edible fruit appears to have been first accomplished by Clemens Kleber (*Am. Perfumer*, 1913, vii., 235), who has shown by exact analytical data that ripe bananas contain amyl acetate, and, so far as known to us, this has remained to the present time the only recorded instance in which the chemical identity of a natural fruit flavour has been determined.

Although amyl valerate is designated in most chemical text-books as "apple-oil," there appears to be no evidence that this compound has ever actually been found in the apple. So far as can be ascertained from a survey of chemical literature, the only published references to the odorous constituents of apples are contained in two brief communications by C. Thomae (*J. prakt. Chem.*, 1911, lxxxiv., 247; 1913, lxxxvii., 142), who has noted that when fresh apple parings are mixed with water and distilled in a current of steam a little solid substance passes over, while occasionally some oil drops are formed which soon for the most part solidify. By extracting the distillate with ether, a solid mass was obtained, which on the addition of a little alcohol became crystalline. After separating the crystals by filtration the liquid yielded a yellowish oil which had the odour of apples. Other experiments were made by extracting fresh apple parings with ether, whereby wax-like substances and some drops of yellowish oil were obtained. The author does not state the quantity of material employed, and no product of the investigation was further characterised or identified.

Experimental.

The material employed in the present research was generously provided by Mr. L. C. Corbett, in charge of horticultural and pomological investigations of the Bureau of Plant Industry, and consisted of fruit grown on the experimental farm

* From *Journal of the American Chemical Society*, July, 1920.

at Arlington, Va. To him and all others of the above-mentioned Bureau of the Department of Agriculture who so kindly placed at our disposal the facilities for preparing and distilling the material our warmest thanks may here be expressed.

PART I. Examination of Ben Davis Apples.

The variety of apple first examined was that known as the Ben Davis, as this was available in considerable quantity, and as the odorous constituents appear to be contained chiefly in the outer skin or rind of the fruit, only the parings were employed. The apples had been stored in a cellar without refrigeration, and at the time of distillation, in the latter part of October, had developed considerable odour. They were pared by means of a machine, which was so adjusted as to completely remove the rind with only a very small portion of the white substance of the apple, and without removing the core, so that any admixture of seeds was carefully excluded. In order to avoid any possibility of fermentation or loss of volatile substances the fresh parings were brought immediately into a still, and, without any further addition of water, subjected to distillation in a current of steam. The total amount of parings employed from the above-mentioned variety of apples was about 161 kg., representing approximately 805 kg. of the entire fruit. The amount of aqueous distillate collected was 163 litres. This distillate was somewhat opalescent, and the first portions separated some oily drops, but on keeping for a few days it became perfectly clear, with the separation of a little solid material on the sides of the glass vessels containing it. The liquid possessed in a high degree the pleasant, characteristic odour of fresh, ripe apples, and even the first portions of the distillate were perfectly neutral to test-paper. After decanting the aqueous liquid, the above-mentioned solid material was dissolved by means of ether, the ethereal solution dried with anhydrous sodium sulphate, and the solvent evaporated. A small amount (0.04 grm.) of a colourless, flocculent substance was thus obtained, which was soluble in hot alcohol, but separated for the most part on cooling. When collected on a filter, and dried on a porous plate, it formed thin, satiny laminæ, which were not altered by contact with either conc. nitric or sulphuric acid. The substance melted quite sharply at 63° and was probably slightly impure triacontane, $C_{30}H_{62}$, which is stated to melt at 65.6°.

Concentration of the Distillate. Identification of Furfural and Acetaldehyde.

A large portion of the original aqueous distillate, amounting to 106 litres and representing 107 kg. of apple parings, was repeatedly cohobated in a current of steam, whereby the odorous substances were eventually concentrated in a volume of about one litre, the nearly odourless liquids remaining from this treatment being reserved for further examination. The concentrated distillate, which was practically neutral and contained some globules of colourless oil floating on the surface, was first subjected to some special tests. It gave no coloration with ferric chloride, indicating the absence of phenolic substances, but rapidly reduced an ammoniacal solution of silver oxide in the cold, producing a metallic mirror, and also

gave an immediate red coloration with sensitised Schiff's reagent, which was evidence of the presence of an aldehyde (Mulliken, "Identification of Pure Organic Compounds," 1905, i., 15. A few drops of the liquid gave with aniline and hydrochloric acid the bright red coloration characteristic of furfural, the latter having doubtless been produced in the process of distillation. When tested for formaldehyde by means of phenylhydrazine hydrochloride a perfectly negative result was obtained (*Z. Nahr. Genussm.*, 1902, v., 353, and *J. Assoc. Official Agr. Chemists, Methods of Analysis*, 1916, p. 147). On the other hand, the distillate gave the specific reaction for acetaldehyde, which consists in adding to a little of the liquid in a test-tube one or two drops of a solution of dimethylamine (33 per cent) and subsequently about 5 drops of a freshly prepared 1 per cent aqueous solution of sodium nitroprusside, when a beautiful indigo-blue colour is produced, soon changing to brown or yellow. Rimini (*Annali Farmacoterapia e Ch.*, 1898, p. 249; *Chem. Centr.*, 1898, Bd. II., p. 277) has shown that the reaction for acetaldehyde as obtained by Simon (*Compt. Rend.*, 1897, cxxv. 1105; *J. Chem. Soc.*, 1898, lxxiv., II., 315) with trimethylamine was due to the presence in the latter of dimethylamine, and that it is given by all secondary bases of the aliphatic series or by ring compounds which have completely lost their aromatic character by hydrogenation. We have found that the above-mentioned blue coloration is readily obtained with a solution of one part by weight of acetaldehyde in 10,000 parts of water, but that it is not produced by formaldehyde, the higher fatty aldehydes, such as *n*-heptylic aldehyde, or by aliphatic terpene aldehydes, such as citral, which gives only a reddish colour. Further confirmation of the presence of acetaldehyde, and evidence of its occurrence as an emanation from ripe apples will subsequently be described.

Hydrolysis of the Esters Contained in the Concentrated Distillate. Identification of Amyl Alcohol and Formic and Caprylic Acids.

The previously mentioned concentrated distillate, amounting to about one litre, was brought into a flask provided with an inverted condenser, 25 grms. of pure sodium hydroxide added, and the mixture kept in active ebullition for 2 hours. During this operation the liquid acquired a deep yellow colour, and a small amount of material separated, which evidently consisted of the so-called aldehyde resin. After cooling, the contents of the flask were distilled in a current of steam, and about 300 cc. of liquid was collected. This liquid, which gave no reaction for aldehyde, possessed a pleasant odour, and after a short time an appreciable amount of yellowish, oily drops separated on the surface. It was extracted five times with pure, aldehyde-free ether, and the neutral aqueous liquid then reserved in order to test for the presence of methyl alcohol, as subsequently described.

(It is known that acetaldehyde when heated with a caustic alkali is chiefly converted into the so-called aldehyde resin, and that small amounts of formic and acetic acids are also produced, together with some odorous substances which may be extracted from the distilled liquid by means of ether. The formation of these products has been duly considered when necessary in the

present investigation in order to exclude any incorrect deductions).

The above-mentioned ethereal liquids were united, dried with anhydrous sodium sulphate, and the greater part of the ether removed by distillation, the residual liquid being then brought into a small, tared flask and allowed to evaporate spontaneously until the odour of ether had disappeared. A yellowish, oily liquid was thus obtained, which had a distinct odour of amyl alcohol, and produced the characteristic irritating effect of the latter on the throat when inhaled. The amount of this liquid was 0.7063 grms., which represented 0.00065 per cent of the weight of apple parings employed. It was brought into a strong flask provided with a tightly-fitting glass stopper, 25 cc. of a chromic acid mixture (*J. prakt. Chem.*, 1892, xlv., 599) added, and the whole heated for 15 minutes on a water-bath at a temperature of about 90° with occasional agitation. The flask was then cooled, the contents diluted with water, transferred to a separatory funnel, and the acid liquid extracted five times with pure, aldehyde-free ether. The united ethereal liquids, after being washed with a little water, were extracted four times successively with 25 cc. of a 5 per cent solution of barium hydroxide. The total alkaline liquid was treated with carbon dioxide for the removal of the excess of baryta, and, after filtration, the neutral liquid was concentrated to a small volume.

(To be continued.)

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Journal de Pharmacie et de Chimie. Vol. xxii., 7th Series, No. 4, August 16, 1920.

ACTION OF HYDROCYANIC ACID ON GLUCOSE. KILIAN'S REACTION.—MM. J. Bougault and J. Perrier.—According to Emil Fischer (*Liebig's Annalen*, 1892, cclxx., 64), the synthesis of oxyacids by the action of hydrocyanic acids on aldehydes is due to the work of Winkler (about 1830). This reaction has been applied to the sugars (glucose, &c.), by Kiliani (*Ber.*, 1885, xviii, 3168), by whose name the reaction is known, although it was a French chemist, Schützenberger (*Bull. Soc. Chim.* [2], 1881, xxxvi., 144), who first showed that inverted sugars, when subjected to the action of hydrocyanic acid and water, give rise to acids containing seven atoms of carbon, according to the equation—

$C_6H_{12}O_6 + CNH + 2H_2O = C_6H_{12}O_6 \cdot CO_2NH_4$. . .
The above authors have further investigated this reaction, and have discovered that alkalinity and acidity play an important part in the success of the operation. In a very faintly acid solution the reaction does not take place, likewise it fails in neutral solution. But it is difficult to lay this latter point down definitely as it is very difficult to obtain an exactly neutral solution, the alkalinity of the glass vessel being sufficient to act as a catalyst. From the above remarks, the authors infer that it was a cyanide and not hydrocyanic acid which plays the active role in the reaction. By writing the equation in the following manner $C_6H_{12}O_6 + CNK + 2H_2O = C_6H_{12}O_6 \cdot CO_2K + NH_3$. . .

these facts can be stated; it can be seen that the quantity of alkali taking part in the reaction as cyanide reappears in an equivalent quantity as ammonia on the right-hand side of the equation. This ammonia gives rise to a further quantity of cyanide, which combines as before with a fresh quantity of glucose, and so on.

NOTES.

At the Machine Tool Trades Exhibition to be held at Olympia in September, a great Convention will be held under the joint auspices of the Home Office and the British Industrial "Safety First" Association. There will be two sessions, at which papers of absorbing interest will be discussed.

ALCOHOL FUEL PATENTS.—*Warning to Investors.*—The Empire Motor Fuels Committee of the Imperial Motor Transport Council has recently been considering the abnormal and unhealthy activity shown by pseudo-inventors in respect of alcohol motor fuels and mixtures containing alcohol. Shortly before the House rose, Mr. E. Manville, M.P., at the request of the Empire Motor Fuels Committee, addressed the following question to the President of the Board of Trade: "If the Patent Office will pay special attention to the number of applications for letters patent in respect of admixtures of such bodies as alcohol, ether, kerosene, benzol, and toluol, as motor fuels, in which applications no element of novelty, discovery, or invention appears to be disclosed; and if he will give instructions to the Patent Office to be especially careful not to hamper or prejudice the production or utilisation of new motor fuels by the creation of ground for litigation in respect of alleged master patents." Sir Robert Horne's reply was that "Full and proper consideration will be given to all applications for patents in respect of inventions relating to new motor fuels before the patent is granted. The Comptroller of the Patent Office in considering what is a proper subject of a patent, is, of course, bound by the provisions of the Patents and Designs Act in accordance with which he must act." It is felt by the Empire Motor Fuels Committee that great damage may be done to the prospect of early production and marketing of new motor fuels if disregard is shown by the Patent Office for the known miscibility within various limits of alcohol, benzol, petrol, and other hydro-carbons and carbohydrates, and the Committee wishes to give warning to the investing public that any claim to a master patent should in any conceivable circumstances be viewed with the maximum of doubt. The Committee feels it is regrettable in the public interests that the Patent Office should be allowing patents to be granted for mixtures which every chemist knows can be employed as fuels and which every engineer knows are more or less applicable in existing engines or in engines slightly adapted in order to suit such mixtures.

ADVERTISING EXHIBITION.—An International Advertising Exhibition will be held in the great entrance halls of the White City, London, from November 29 to December 4. The buildings have an area of over 200,000 square feet, and it is evident that the whole space will be occupied by interesting and novel demonstrations of the power

of modern advertising as an instrument of salesmanship. Those interested should write at once to the Administrator, Mr. Sam G. Haughton, 167, Strand, London. The Government, particularly the Board of Trade, is actively interested in this endeavour to aid the commerce of the Empire and so are the trades commissioners of our Colonies, while foreign countries are evincing a keen desire to be represented. For the first time the whole of the complex science of advertising in its every phase will be revealed in such a way as to interest not only the expert, the manufacturer, and the distributor, but also the man in the street. The Exhibition will be open to everyone and it is confidently expected that many thousands of people will visit the White City palaces during the week. The profits are to be divided among the charities associated with the printing and allied trades.

NOTICES.

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Applications stating age, experience, war service (if any) etc., should be addressed to the Medical Officer of Health, No. 2, Savoy Hill, W.C.2., so as to reach him not later than Monday, 27th September, 1920.

JAMES BIRD,
Clerk of the London County Council

UNIVERSITY OF DURHAM. ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE.

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THIS Scholarship, of the value of £100, for one year, together with a prize books, will be awarded in October, 1920, on the results of an examination in Chemistry, with Crystallography or Mineralogy. Candidates must be Bachelors of Science of any British University of not more than 3 years standing from the date of graduation. Further particulars may be obtained on application to the REGISTRAR, Armstrong College, Newcastle-on-Tyne.

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THE Proprietors of the Patent Nos. 108889 and 108807 for

"IMPROVEMENTS IN OR RELATING TO APPARATUS FOR GENERATING GAS" AND "PROCESS OF GENERATING HYDROCYANIC ACID GAS"

are desirous of entering into arrangements by way of licence and otherwise on reasonable terms for the purpose of exploiting the same and ensuring their full development and practical working in this country. All communications should be addressed in the first instance to

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3153.

LUBRICATION AND THE GERM PROCESS.*

By HENRY M. WELLS and JAMES E. SOUTHCORBE, M.Sc.

THE authors draw attention that the modern view of lubrication on the physico-chemical side is the existence of a residual valency or affinity between the oil and the solid surfaces of the bearing and journal. The problem has therefore to be considered as a kind of intimate relationship between the oil and the metal. This is quite a different view to that held by investigators in the past, who thought that the property of "oiliness" so strongly manifested by fatty oils as compared with mineral oils resided in some particular physical characteristic of the oil itself.

The modern point of view has been elaborated recently by a number of students of the subject.

The authors have discovered the "reason" why the fatty or fixed oils possess superior friction-reducing properties to that of mineral oils. They have shown that this is due essentially to the presence in fatty oils of minute quantities of free fatty acids, which are absent in the majority of mineral oils. In consequence of this discovery, they have added small quantities (about one per cent) of fatty or organic acids, which are easily accessible and relatively cheap to mineral hydrocarbon oils. The products so obtained possess remarkably low frictional co-efficients. As an example, the addition of 2 per cent of common fatty acid to a mineral hydrocarbon oil reduces the coefficient of friction shown by this oil on a friction testing machine from 0.0084 to 0.0052—a diminution of 25 per cent.

By suitably choosing the type of fatty acid to be added to mineral oil the behaviour of oils in the presence of water and other contaminating substances can be modified at will. It is also shown that the risk of metallic corrosion is even less with these oils than with the usual compounded oils, because the latter frequently develop in working notable quantities of free acid.

The principle of making mineral lubricating oils possessing increased frictional reducing properties by adding to mineral oils suitably chosen fatty acids in relatively minute amounts has been patented throughout the world, and has been somewhat fancifully called the "Germ Process," because the fatty acid is the germ of the idea.

The value of the process lies in that oils possessing friction-reducing properties much superior to mineral oils can be prepared at relatively little extra cost to mineral oils.

Secondly, by this means an immense quantity of fatty oil suitable for the manufacture of margarine and other food-stuffs is liberated for the country's needs and substituted by a much smaller amount of commercial fatty acids, which are quite unsuitable for food and are more or less in the nature of a by-product.

* Abstract of Paper read before the British Association (Cardiff Meeting), Section B.

Finally, it may enable the lubricating oil manufacturer to produce the highest class of friction-reducing oils from comparatively thin—therefore cheaper—mineral oils, and incidentally this may have the utmost significance to-day when we are striving to foster and develop the mineral oil production of our own country and the Empire.

FUEL ECONOMY.*

Introduction.

THE Committee has held altogether six meetings since its reappointment last year, and is investigating (*inter alia*) the following matters, namely:

(a) The present official methods of arriving at coal mining statistics (*e.g.*, outputs of coal, &c.) in this and other coal producing countries.

(b) The effect of the war upon the British coal export trade.

(c) The chemical constitution of coal.

(d) The low temperature carbonisation of coal.

(e) The thermal efficiencies at present attainable (i.) in the carbonisation and gasification of coal by various systems, (ii.) in domestic fires and heating appliances, (iii.) in metallurgical and other furnaces, (iv.) in steam raising and power production, and (v.) in regard to the generation of electric power in public stations.

(f) Sources of supply of liquid fuels.

Although the Committee has made satisfactory progress with its inquiries in certain directions during the past year, both time and opportunity have been wanting for completing them. The present Report,† therefore, is of an interim nature, but the Committee hopes to report more fully on the above matters to the Edinburgh Meeting next year.

Coal Mining Statistics.

The attention of the Committee having been drawn by Professor Henry Louis to the fact that, owing to considerable variations in the modes of arriving at the official data concerning coal outputs, &c., periodically published by Government Departments in the various coal producing countries, it is impossible to regard them as being properly comparable, the Committee requested him to prepare a Memorandum on the subject. This he subsequently did, and, having regard to the great importance of the matter, the Committee decided to publish the Memorandum *in extenso* as Appendix I. to this Report, in the hope that it may lead to the desired reform being effected. In particular, the Committee endorses Professor Louis' view concerning the importance of summoning an International Conference for determining the precise manner in which mineral statistics of all kinds shall be collected, tabulated, and finally issued to the public.

*Read before the British Association (Cardiff Meeting), Section B

† Third Report of Committee (Prof. W. A. Bone* (Chairman), H. James Yates* (Vice-Chairman), Robert Mond* (Secretary), A. H. Barker, Prof. P. P. Bedson, Dr. W. S. Boulton, E. Bury, Prof. W. E. Dalby, E. V. Evans, Dr. W. Galloway, Sir Robert Hadfield, Bart., Dr. H. S. Hele-Shaw, Dr. H. Helps, Dr. G. Hickling, Dr. V. Hollingsworth, A. Hutchinson, Principal G. Knox, Prof. Henry Louis, H. M. Morgans, W. H. Patchell, A. T. Smith, Dr. J. E. Stead, C. E. Stromeyer, G. Blake Walker, Sir Joseph Walton, M.P., Prof. W. W. Watts, W. B. Woodhouse, and C. H. Wordingham*) appointed for the Investigation of Fuel Economy, the Utilisation of Coal and Smoke Prevention. —*Denotes a Member of the Executive Committee.

Coal Outputs and Average Pithead Prices in 1919.

According to information kindly furnished to the Committee by the Statistical Department of the Board of Trade, the total output of coal in the United Kingdom during the year 1919 has been provisionally estimated at 229,668,000 tons, and the total output per person employed (below and above ground) in the mines at 197.5 tons.

Owing to abnormal circumstances during the period of coal control, it is difficult to give strictly comparable figures for the average pithead prices of coal in the years immediately preceding and following (respectively) the war. According to official estimates supplied by the Statistical Department of the Board of Trade, the pithead prices per ton of coal raised in 1913, and in July, 1919, respectively, were approximately as follows:

	Average for 1913		On July 16, 1919	
	s.	d.	s.	d.
Labour	6	4	19	5½
Timber and Stores ...	1	0	3	2½
Other Costs	0	11	1	2½
Royalties	0	5½	0	6½
Owners' Profits	1	5	1	2
Compensation	—	—	0	3½
Administration, &c. ...	—	—	0	2½
Total	10	1½	26	0½

In the Report recently made to the Prime Minister by Messrs. Alfred Tongue & Co., Chartered Accountants, of Manchester and Glasgow, and presented to Parliament by command of His Majesty (Cmd. 555), it was estimated that the average cost per ton of coal raised in British mines during the year ending March 31, 1920, was as follows:—

	s.	d.
Wages	19	7½
Timber and Stores ...	3	10
Other Costs	1	6
Royalties	0	6½
Administration	0	1
Capital Adjustments under Finance Acts	0	4
Control and Contingencies ...	0	2
Owners' Profits	1	2
Total	27	3½

It would thus appear that the pithead cost of coal has been nearly trebled as the result of the war.

Coal Export Statistics.

The Statistical Department of the Board of Trade has also placed at the disposal of the Committee detailed information concerning the amounts of coal exported from the principal ports of the kingdom (a) to British possessions, and (b) to foreign countries, during each of the years 1913-1919 inclusive. In view of the importance of such statistics, the Committee has decided to publish them in tabular form as Appendix II, to this Report. The Committee is also collecting information as to average prices obtained at the principal ports for the coal exported during each of the years in question. In the light of such statistics the Committee hopes next year to be able to review the question of the effect of the war upon the coal export trade.

Chemistry of Coal.

During the year considerable progress has been made with the researches on the chemistry of coal under the direction of Professor Bone at the Fuel Laboratories at the Imperial College of Science and Technology, further details of which will shortly be published. The Committee has also followed with close attention the work recently published (a) by Drs. Marie Stopes, R. V. Wheeler, and Rudolph Lessing upon the four macroscopically distinguishable portions of banded bituminous coal and their respective behaviour on carbonisation and oxidation, (b) by Mr. S. R. Illingworth at the Treforest School of Mines, and (c) by Mr. F. S. Sinnatt and collaborators of the Lancashire and Cheshire Coal Research Association.

Future Standards of Gas Supplies.

Since it reported its views on the above subject to the Bournemouth Meeting of the Association last year, the Committee has followed upon the matter, and on February 2 last, a deputation, consisting of the Chairman, Sir Robert Hadfield, Messrs. W. H. Patchell and H. James Yates, waited upon the then President of the Board of Trade (the Rt. Hon. Sir Auckland C. Geddes, K.C.B.) to lay before him the views of the Committee upon the subject, with special reference to impending legislation.

In introducing the deputation, Professor Bone called the attention of the President to (a) the Report on Gas Standards which had been made by the Fuel Research Board, (b) the conclusions thereon that had been arrived at as the result of a conference between representatives of consumers, local authorities, and gas undertakings, and (c) the announcement by the President of the Board of Trade that a Bill would shortly be introduced in Parliament to give effect to the recommendations of the Fuel Research Board. (The Bill was subsequently introduced by Sir Robert Horne in the House of Commons on May 19, 1920). He explained that the Committee had looked at the question primarily from the view of the national interests as a whole, and particularly from that of domestic and industrial gas consumers. It agreed with the Fuel Research Board that the future basis of charge to the consumer should be the actual number of thermal units supplied to him in the gas which passed through his meter, but desired that the charge should be based upon the "ascertained net calorific value" of the gas supplied rather than its "declared calorific value," as proposed by the Fuel Research Board. It also endorsed the Fuel Research Board's original recommendation that the gas should be supplied at a pressure of "not less than two inches of water at the exit of the consumer's meter," but expressed its disagreement with the Board's subsequent view that the pressure condition might be reduced to one of "not less than two inches of water in any main or service pipe of two inches in diameter"; because what mattered to the consumer was the adequacy of the pressure in his own pipes rather than in the gas mains outside his premises.

It was also stated that the Committee attached great importance to the pressure being maintained as constant as possible, as well as to gas undertakings being required to pay greater attention than ever to the removal of cyanogen and

sulphur impurities from the gas. Finally, it was explained that the Committee, whilst agreeing generally with the proposals in regard to the new thermal basis for the sale of gas, and to the restriction of its inert constituents, considered that its chemical composition would need some statutory regulation, and that in particular no public gas supply should be allowed to contain less than 20 per cent of methane or more than 20 per cent of carbon monoxide.

After Sir Robert Hadfield had endorsed the views of the Committee from the point of view of industrial consumers of gas, Mr. H. James Yates outlined his views as a maker of gas fires, who had for many years given much attention to the scientific investigation of domestic heating and ventilation. He laid stress upon the importance of maintaining a constant pressure of not less than two inches water gauge on the consumer's side of the service pipes, and that the gross calorific value of the gas supplied should not be allowed to fall below 450 B.Th.U. per cubic foot, stating that if gas undertakings supplied gas of lower calorific value a large part of the existing gas appliances would become useless.

Sir Auckland Geddes, in his reply, promised to give full consideration to the facts and opinions which they had laid before him. Also, he said that he had been impressed with the physiological side of the question and with the danger of cyanogen and of too high a proportion of carbonic oxide in gas.

The "Gas Regulation Bill," as subsequently presented to the House of Commons on May 19 last by Sir Robert Horne (the new President of the Board of Trade), contained far-reaching new proposals concerning the public sale and distribution of gas, among which the following are of especial importance to consumers:—

(a) That the Board of Trade may, on the application of any gas undertakers, by order, provide for the repeal of any enactments or other provisions requiring the undertakers to supply gas of any particular illuminating or calorific value, and for substituting power to charge for thermal units supplied in the form of gas.

(b) That where such substitution has been decided upon, the new basis for the sale of gas shall be 100,000 British Thermal Units (to be referred to in the Bill as a "therm"). The consumer will then be charged according to the number of "therms" supplied to him in the gas, and the standard price per therm fixed by the order shall be a price corresponding, as nearly as may be to the price fixed by former provisions for each 1000 cubic feet, but with such additions (if any) as appear to the Board to be reasonably required in order to meet unavoidable increases since June 30, 1914, in the costs and charges of and incidental to the production and supply of gas by the undertakers; and the order may make such modifications of any provisions whereby the rate of dividend payable by the gas undertakers is dependent on the price of gas supplied as appear to the Board to be necessary.

(c) That an order under the Act shall prescribe the time when, and the manner in which, the undertakers are to give notice of the calorific value of the gas they intend to supply (*i.e.*, "declared calorific value"), and shall require the

undertakers, before making any alteration in the declared calorific value, to take at their own expense such steps as may be necessary to alter, adjust, or replace the burners in consumers' appliances in such manner as to secure that the gas can be burned with safety and efficiency.

(d) That the gas supplied under the Act (i.) shall not contain any trace of sulphuretted hydrogen, (ii.) shall not be at a pressure of less than two inches water-gauge in any main or service pipe of two inches diameter or upwards, and (iii.) shall not contain more than a certain permissible proportion of incombustible constituents (namely, 20 per cent during a period of two years after the passing of the Act, 18 per cent during the succeeding two years, and 15 per cent thereafter).

(e) That as soon as may be after the passing of the Act the Board shall cause an enquiry to be held into the question whether it is necessary or desirable to prescribe any limitations of the proportion of carbon monoxide which may be supplied in gas used for domestic purposes, and may, if on such inquiry it appears desirable, make a special order under the Act prescribing the permissible proportion.

(f) That Gas Referees and Examiners shall be appointed for the purpose of (i.) prescribing the apparatus and method of testing the gas, and (ii.) carrying out of such prescribed tests.

During the passage of the Bill through its Committee stage in the House of Commons, the important sub-section limiting the amount of incombustible constituents permissible in gas (*vide* (d) (iii.) above) was deleted, on the understanding that, subsequent to the passing of the Act, the matter shall be made the subject of an official inquiry by the Board of Trade. The effect of this amendment is, therefore, to put the question of "inerts" into the same category as that of carbon monoxide, and the whole matter now stands as follows:—

The Board of Trade shall, as soon as may be after the passing of this Act, cause inquiries to be held into the question whether it is necessary or desirable to prescribe any limitations of the proportion of carbon monoxide which may be supplied in gas used for domestic purposes, and into the question whether it is necessary or desirable to prescribe any limitations of the proportion of incombustible constituents which may be supplied in gas so used, and may, if on any such inquiry it appears desirable, make one or more special orders under this Act prescribing the permissible proportion in either case, and any such special order may have effect either generally or as regards particular classes of undertakings, and the provisions of the special order shall have effect as if they were enacted in this section.

When such official inquiries are instituted by the Board of Trade this Committee will hope to be given an opportunity of presenting again its views (as already reported) upon the matters concerned.

Alcohol from Coke Oven Gas.

During the past year a notable development has been made in connection with the technology of by-product recovery from coal as the result of Mr. E. Bury's successful experimental trials, in conjunction with Mr. O. Ollander, at the Skinninggrove Iron Works, upon the absorption of ethy-

lene from debenzolised coke oven gas and its conversion into ethyl alcohol. These trials have demonstrated the possibility of obtaining on a large scale 1.6 gallons of absolute alcohol per ton of the particular Durham coal carbonised. Assuming a similar yield from the 15,000,000 tons (or thereabouts) of coal now annually carbonised in British by-product coke ovens, it is claimed to be possible to obtain from coke works alone a 95 per cent industrial alcohol in quantities equivalent to about 24 million gallons per annum of the absolute spirit.

Although a full account of the investigation has already been given by Messrs. Bury and Ollander in a paper before the Cleveland Institution of Engineers in December last (*vide also Iron and Coal Trades Review*, December, 1919), the Committee, whilst not expressing any opinion as to the commercial prospects of the process, considers that the technical importance of it is such as to warrant attention being drawn in this Report to some of its salient features (see Appendix III).

The Committee recommends that it be re-appointed to continue its investigations with a grant of £35.

APPENDIX I.

Memorandum upon Coal Mining Statistics.

The most important statistics concerning coal are the figures giving the annual production of coal, the number of workers employed in the mines, the number of fatal and of non-fatal accidents respectively. These statistics are collected and published by the Government Departments in most coal-producing countries, and upon these are based a number of comparative statements by which the progress of the industry in different countries is usually estimated, such as the production per worker employed, the accident death-rate per thousand workers, &c. For most economic and social studies, the number of workers employed is in several respects the most important of these figures, and unfortunately it would appear to be the one upon which the least dependence can be placed. Elaborate reports have been drawn up, and legislation has even been enacted, based upon the comparative results of these data; and it has been quite freely assumed that the figures given for different countries or different districts of a country are properly comparable, whilst as a matter of fact the methods of arriving at these figures vary so widely that they come to bear quite different meanings, and the assumption that similar headings always connote similar interpretations is utterly without foundation.

Production.—In this country the returns of the output of coal until recently included the stones and dirt sent up to bank with the coal and picked out on the belts or screens; since that time the weight of coal alone is supposed to be returned. The instructions at present issued by the Home Office read as follows:—

The weight given should be the net weight after screening or sorting. . . . Where the net weight of the coal is not determined during the year in respect of which the return is being made, it will be sufficient if a deduction is made according to the average percentage of dirt extracted from the coal at the mine. In cases where the coal is sold as it leaves

the pit without screening or sorting it will be proper to give the gross weight sent out of the pit as the amount of output.

It will be seen that the instructions are somewhat vague, and that they also leave considerable openings for guess-work and estimates instead of accurate facts; furthermore, the instructions would in some cases at any rate compel the inclusion of washery dirt under the heading of output, since this dirt does not always come under the heading of "dirt extracted from the coal at the mine." It is by no means uncommon for one company to control two collieries not far distant from each other and to erect at one of them a washery to which the small coal from the first colliery is to be sent for washings; in such a case if the instructions are literally followed, washery dirt will be included in the returns of the coal output from the first colliery and excluded from the second. Accordingly it is natural that the practice in making up these returns varies greatly from district to district, and even from colliery to colliery. In some cases both the dirt picked out on the belts and that washed out in the washery are deducted from the pithead weight, *i.e.*, from the tonnage on which the men are paid; in other cases no deduction at all is made for washery dirt, and in yet other cases an arbitrary percentage is deducted from the coal sent to the washery. There is also some difference as regards the practice concerning "free coal" given to the miners and coal for colliery consumption. In most cases all this coal is returned as part of the production; in some cases the coal consumed by the pits is not included, and apparently in a few cases both the "free coal" and coal for colliery consumption are deducted from the output. In some places it is customary to give as a return of output the landlord's tonnage, that is the amount on which royalty is paid, which is usually the output less certain deductions allowed by the terms of the lease. In view of this wide variation, it would be a distinct advantage if the Home Office were to issue specific instructions on all the above points, so as to secure uniformity of method in making returns throughout the United Kingdom. The methods used in Canada might well be adopted here.

In Canada a more definite system is adopted; the introduction to the Canadian Annual Statistics states in definite language what is intended, as follows:—

The term "production" in the text and tables of this report is used to represent the tonnage of coal actually sold, or used, by the producer, as distinguished from the term "output," which is applied to the total coal extracted from the mine, and which includes, in some cases, coal lost or unsaleable or coal carried into stock on hand at the end of the year.

Apparently throughout Canada the various Provinces issue sheets which have to be filled up every month, and which the different Provincial Governments have agreed to issue in identical form, so that returns for the Dominion can be made by the Canadian Department of Mines or by the Dominion Bureau of Statistics. The whole of the collection of statistics, and, in fact, the administration of mining law, is controlled by the respective Provincial Governments, with the exception of mining lands in certain of the Western Pro-

vinces and North-West Territories, which are controlled directly by the Dominion Government. These monthly returns show the amount of free coal or of coal sold to miners at a reduced price, the quantity used for colliery consumption, specifying any used on the colliery company's own railways, the quantity of coal used for making coke and briquettes, the quantity stocked, and the quantity on hand. The only fault that can be found with these returns is that they do not specifically ask for a return of the dirt picked out and washed out respectively. In Canada the term "production" is restricted to marketable or economically useful coal, whilst the term "output" is the equivalent of what we sometimes speak of in this country as "drawing," *i.e.*, everything drawn out from the colliery, inclusive of any dirt that may be extracted subsequently.

In the United States the production means the total production of clean coal, that is to say, coal with the exclusion of pickings and washery dirt, and including colliery consumption. The work is done by the Mineral Resources Division of the United States Geological Survey, but there is a good deal of overlapping and difficulty owing to some of the statistics being collected by State Bureaux and others by Federal Bureaux; in this respect attention may be directed to the Conference on this subject held at Washington in 1916, the results of which are printed in a report of the Committee on the Standardisation of Mining Statistics in 1918. At present cards in the shape of card slips are issued, to be filled up annually, and these ask for the total production which is defined to "include all marketable coal, excluding only refuse from washeries and slack coal wasted." It distinguishes between the coal loaded at the mine for shipment, coal used locally, colliery consumption, and coal used for making coke at the mine. It will be seen that these instructions are fairly clear and definite.

In France the production includes the whole of the drawings, deducting only the worthless waste, *i.e.*, pickings and washery refuse.

In Belgium the same practice is followed, the production including colliery consumption and coal given or sold to employees, but definitely excluding pickings and washery waste.

It will be seen that all these producing countries are aiming at one definite meaning for the word "production," and in this respect there is at any rate uniformity of intention. Unfortunately the execution of the object leaves much to be desired. The Canadian practice of monthly returns has much in its favour; it no doubt throws a certain amount of additional work both upon individual collieries and upon the department collecting statistics, but, on the other hand, it enables half- and quarterly statements to be issued very shortly after the conclusion of the respective periods, and in the same way annual statements can be produced much more rapidly than would be the case if the whole of the returns began to come in after the end of the year. It is quite desirable that the returns should show definitely the total weights of drawings, the weight of dirt picked and washed out, the weight given or sold to employees, the colliery consumption, and the coal used for making coke. Again, there would not be a great deal of labour involved in keeping these figures, and the information would be of the greatest value.

Number of Employees.—In this country the only information asked for is a return "of persons ordinarily employed"; the returns specify that it must include all the persons employed on the mine premises, such as officials, storekeepers, clerks, &c., those employed on the pit sidings, on private branch railways and tramways, and in washeries adjacent to and belonging to the mine. Furthermore, the number employed underground must be kept separate from those employed above-ground, and there is also a separation according to age and sex. There is, however, no information as to what is meant by the "number of persons ordinarily employed," although this is evidently the crux of the whole matter. The consequence is that extremely variable methods are made use of. Some pits merely give the number of men entered on the pay sheet for the particular day in the year on which the return is made out; others take two or three days which they consider normal and average these. Some return the number of employees on the books of the company, others the number on the time roll; with the prevailing amount of absenteeism, the former number will exceed the latter by about 25 per cent, but there is no instruction as to which of the two is the figure intended to be given. Some of the more painstaking collieries average the number of men employed daily, but this is apparently exceptional. It is evident that a more definite and systematic method would have to be adopted before it is possible to attach anything like a precise meaning to returns of numbers employed in this country.

In Canada, apparently, monthly returns are made, and these are averaged for the year. The Canadian intention is to "show the actual amount of labour in terms of days worked, rather than the actual number of individual men that may have been engaged," and this is obviously the correct way of dealing with the subject. The returns ask for a classification under eight different heads and separate them into underground and above-ground workers; it may be noted that in Canada the number of men employed at the coke ovens and briquetting plants in connection with collieries is included in the mine employees, whilst according to the wording of the English return these should be excluded in this country, although there is no warranty for saying that the instructions for making the latter returns are in all cases strictly complied with. Furthermore, in Canada there is an interesting table showing the time lost through absenteeism, meaning thereby the fault of the men and through a series of other reasons which may be classified as the fault of the mine or of the industry. It would be a distinct advantage if such returns were available for this country.

In the United States of America the information asked for is the average number of men employed during the year excluding the coke workers and office force. In the exclusion of the latter item this return differs from the British return; in the exclusion of the former item it differs from the Canadian return. The number of hours per working day is also asked for, as well as the average number of days lost by strikes and the number of men thereby affected. The intention in America is to get the average number of men employed during the year, but apparently the methods of obtaining these are about as vague as they are in this country. In the report already referred to it

is stated that "without instruction in regard to the way these averages (average number of employees) should be computed there will be a lack of uniformity of method, and in many cases the figures submitted will not be averages, and will not represent even approximately the real average number of persons employed." No one with any experience of the subject will doubt the accuracy of this statement, and it is certainly applicable to countries other than the United States. In the report in question the definition is put forward that "the average number of men should be the actual number of man-hours for the year." This obviously is a clear and intelligible definition, and it would probably be a great advantage if it were generally adopted.

In Belgium this principle is carried into effect; the number of employees returned represents the quotient of the number of days' work done in the year divided by the number of working days. This figure is thus really the mean number of workmen engaged during the working days.

In France, on the other hand, the number of employees is intended to be the number of names regularly on the colliery pay roll; a column is reserved for the number of days worked in the year. It is obvious that we are dealing here, under the same heading, with two entirely different conceptions; some countries return the number of men who normally get their living by the industry, without any regard to the amount of absenteeism or the length of time that these men may be at work; whilst others return the number of men who have put in a full year's work, meaning thereby have worked on all the days on which the mine was in operation. Obviously, these two figures differ widely from each other, and the fact that both are returned indifferently under the same heading vitiates many of the conclusions that have been drawn upon the basis of these returns.

Fatal Accidents.—It is a curious fact that whereas every coal-mining country publishes a return of fatal accidents, there appears to be in none of them any legal definition of what constitutes a fatal accident. In the absence of legal definition in this country the Home Office has for many years made a practice of classifying all mine accidents which result in death within a year and a day as fatal accidents, apparently for no better reason than that in so doing they have followed the old Coroner's Law.

In Canada, the Mineral Resources Statistics Branch does not collect accident statistics, and these appear to be left to the relative departments of different Provinces. They are not asked for in the statistical returns, but are obtained from the reports to the Inspector of Mines. In the Province of Alberta a fatal accident is construed as an accident which causes death within a twelve-month. In the other Canadian Provinces there appears to be no definition at all, and it would seem that if a man dies from the effect of a mining accident, however long the death may be after the accident, it would apparently be reported as a fatal accident for the year in which the death takes place.

In the United States mine accidents statistics are gathered by the various States and are by no means as reliable as statistics gathered by the Bureau of Mines. Mr. G. S. Rice, the chief

mining engineer of the Bureau of Mines at Washington, gives me the following information: "As to what constitutes a definition of a fatal accident, this varies in the different States. In some States it means immediate death, in others within a day or two, in still others, if the man dies from the direct cause of the accident before the report is turned in, which is in February for the preceding calendar year, which may mean from two to thirteen months after the accident." It will be seen that these figures are obviously vague and unreliable. It is a curious fact that in the report of the Committee on the Standardisation of Mining Statistics already referred to, the terms fatal and non-fatal accidents are freely used, but there is no attempt at definition.

In France the principle followed is that the records of fatal accidents are restricted to those who are mortally injured in a mine accident, that is to say, either those killed on the spot or who dies as the result of their injuries within a few hours after the accident, or at the outside within a few months without ever having been able to resume work. With regard to those whose death, occurring after a considerably longer interval, is the consequence of injuries received, they do not appear on the record, the Statistical Department not being, as a rule, informed of their death, and being, moreover, unable to determine its real cause.

In Belgium, on the other hand, a fatal accident is restricted to an accident that causes death within thirty days.

Here, again, it may be pointed out that this extremely important matter is in a chaotic condition, and that it is most urgent that an agreement be arrived at as to what precisely is meant by a fatal accident.

Non-Fatal Accidents.—Here, again, there is a wide variation to be noted in practice. In this country the return is asked for of non-fatal accidents within any given year, non-fatal accidents being defined as accidents disabling the victim for more than seven days.

In Canada the practice varies in the different Provinces. Apparently in Nova Scotia, a non-fatal accident is classified as an accident by which a man must be disabled for at least seven days, but from which he recovers. In the Province of Saskatchewan accidents entailing a disability of less than six days are not recorded. In Alberta a non-fatal accident must be reported if a man is off for more than fourteen days; apparently in some cases accidents involving a disability of less than fourteen days are tabulated as slight accidents.

In the United States of America the question of what constitutes a non-fatal accident is even more unsettled than the definition of a fatal accident. In some of the States statistics are collected based on the State Compensation Acts, under which compensation is paid for an injury causing a loss of at least two weeks; in metal mines apparently an accident causing a loss of at least one shift is tabulated as a slight injury, and one involving a loss of two weeks as a serious injury.

In France injuries causing disability to work for more than twenty days are counted as non-fatal accidents.

In Belgium all non-fatal accidents are accidents that cause permanent disability, whether this be

total or partial, accidents involving only temporary disability not being included in the returns.

The above can only be looked upon as an attempt to supply a portion of the information which is evidently needed before it is possible to read coal-mining statistics at all intelligently. It will be obvious, however, from what has been said, that attempts at comparisons, which have been so freely made without taking into account the striking differences in interpretation given above, must result in wholly inaccurate comparisons. I sincerely hope that the data here given may be further extended to all coal-producing countries, and I wish to urge again, as I have done in more than one International Congress, the importance of an International Conference for determining the precise manner in which mineral statistics of all kinds shall be collected and tabulated, and the precise meaning that should be attached to the various headings.

HENRY LOUIS.

(To be continued.)

THE ODOROUS CONSTITUENTS OF APPLES. EMANATION OF ACETALDEHYDE FROM THE RIPE FRUIT.*

By FREDERICK B. POWER and VICTOR K. CHESNUT.

(Continued from page 132).

ON the addition of silver nitrate a small amount of nearly colourless precipitate was obtained, which was collected, washed, and dried on a porous tile over sulphuric acid.

Subs., 0.0358: Ag, 0.0185.

Calc. for $\text{AgC}_6\text{H}_5\text{O}_2$: Ag, 51.7. Found: 51.6.

The acid obtained by the oxidation of the above-described hydrolytic product was thus found to be valeric acid, and its formation established the presence of amyl alcohol in the apple distillate.

After extracting the above-mentioned ethereal liquid with baryta it was washed with a little water, dried with anhydrous sodium sulphate, and the ether allowed to evaporate. A small amount of an oily liquid was thus obtained, which was mixed with water and distilled in a current of steam. The first portion of the distillate separated some drops of a fragrant oil, and, assuming it to be an ester, the entire distillate was subjected to hydrolysis with sodium hydroxide and further examined in the manner previously described. The oily product was thus found to consist of amyl valerate, which had been formed together with free valeric acid by the oxidation of the amyl alcohol.

The yellow, strongly alkaline liquid remaining from the hydrolysis and subsequent distillation of the concentrated apple distillate was filtered in order to remove the small amount of aldehyde resin, which, when washed and dried, amounted to 0.063 grms. The liquid was then acidified with sulphuric acid and distilled in a current of steam. About two litres of distillate was collected, the first portions of which had a pronounced odour and acid reaction, and separated a few oily drops. The entire distillate was made alkaline with barium hydroxide, concentrated, filtered, and the excess of baryta removed by carbon dioxide. The

clear, filtered solution of barium salt was found to contain a considerable amount of formate, which was removed by treatment in the cold with a 4 per cent solution of potassium permanganate, a current of carbon dioxide being meanwhile passed through the liquid. After removing the slight excess of permanganate by a gentle heat, and filtering to separate the manganese dioxide, the colourless, neutral liquid was concentrated. It then gave with silver nitrate a small amount of a nearly white precipitate, which was collected, washed, and dried on a porous tile over sulphuric acid.

Subs., 0.0440: Ag, 0.0192.

Calc. for $\text{AgC}_6\text{H}_5\text{O}_2$: Ag, 43.0. Found: 42.8.

This result is thus seen to indicate the presence of caprylic acid, of which further evidence was subsequently obtained. The filtrate from this salt gave no further precipitate with silver nitrate, and no additional amount of a definite silver salt could be obtained from it by concentration. The residue from its evaporation, however, when heated with absolute alcohol and a little conc. sulphuric acid, developed a fruity odour, which was evidence of the presence of small amounts of the lower fatty acids. In addition to the above-mentioned formic and caprylic acids, as obtained in the process of hydrolysis, the identification of other acids in the original distillate will subsequently be described.

It was previously noted that after hydrolysis of the concentrated apple distillate the subsequent distillate from the alkaline liquid was first extracted with ether and then reserved in order to test it for methyl alcohol. This was conducted by first saturating the liquid with common salt, filtering, extracting with light petroleum (b.p. 30-55°), and distilling the salt solution. After repeated concentration of this distillate it was tested according to the method of Denigès (*Recherche de traces de méthanol en présence d'éthanal par la fuchsine bisulfitee*, *Compt. Rend.*, 1910 cl., 529), as elaborated by von Fellenberg (*Biochem. Z.*, 1918, lxxxv., 45), which depends upon the oxidation of methyl alcohol in strongly acid solution to formaldehyde. A reaction was obtained which showed quite definitely the presence of traces of methyl alcohol, and it was ascertained by control experiments that this was not contained in the ether which had previously been employed for extracting the liquid examined. This result was, moreover, confirmed by some special experiments, to be described later, which completely established the occurrence of small amounts of both methyl and ethyl alcohols in apple parings.

Examination of the Aqueous Liquids Remaining from the Concentration of the Original Distillate. Identification of Formic, Acetic, Caproic, and Caprylic Acids.

The large quantity of nearly odourless liquid remaining from the cohobation of 106 litres of the original distillate, together with that obtained by the subsequent concentration of 57 litres of distillate, as later described, was made alkaline with sodium hydroxide and evaporated to a volume of about one litre. It was then acidified with sulphuric acid and distilled in a current of steam. About 5 litres of distillate was collected, the first portions of which were turbid, had a strongly acid reaction, and separated some oily drops. The

* From *Journal of the American Chemical Society*, July, 1920.

entire amount of distillate, which had an odour resembling that of the higher fatty acids, was made alkaline with barium hydroxide and evaporated to a small volume. After filtration the excess of baryta was removed by carbon dioxide and the liquid again filtered and concentrated. It was found to contain a large amount of formic acid, which was removed by treatment with a cold 4 per cent solution of potassium permanganate, a current of carbon dioxide being meanwhile passed through the liquid. After the separation of the manganese dioxide by gently heating and filtering, the colourless, neutral solution was concentrated. By the subsequent addition of silver nitrate a number of silver salts were obtained, which gave the following figures on analysis.

Fraction I. Subs., 0.0139: Ag, 0.0059.
Calc. for $\text{AgC}_2\text{H}_3\text{O}_2$: Ag, 43.0.
Found: 42.4.

This result indicates the presence of a small amount of caprylic acid, which had been found in larger proportion in the products obtained from the concentrated distillate after hydrolysis.

Fraction II. Subs., 0.0370: Ag, 0.0177.

Fraction III. Subs., 0.0457: Ag, 0.0223.
Subs. 0.0394: Ag, 0.0192.
Calc. for $\text{AgC}_8\text{H}_{17}\text{O}_2$: Ag, 48.4.
Found: II, 47.8; III, 48.8, 48.7.

These fractions evidently represented salts of caproic acid, and they all developed the characteristic fatty odour on ignition.

The filtrate from the preceding fractions yielded successively the following additional silver salts.

Fraction IV. Subs., 0.0464: Ag, 0.0284.

Fraction V. Subs., 0.0540: Ag, 0.0342.

Fraction VI. Subs., 0.0489: Ag, 0.0312.

Fraction VII. Subs., 0.0519: Ag, 0.0335.

Fraction VIII. Subs., 0.0632: Ag, 0.0407.

Calc. for $\text{AgC}_6\text{H}_{11}\text{O}_2$: Ag, 64.6.
Found: IV., 61.2; V., 63.3; VI., 63.8; VII., 64.5; VIII., 64.4.

It may be concluded from the above results that the volatile acids of the Ben Davis apple are chiefly formic, acetic, and caproic acids, with a very small amount of caprylic acid. There was no evidence of the presence of valeric acid.

Extraction and Characters of the Essential Oil.

In order to ascertain the general characters of the combined volatile constituents of the apple a portion of the original distillate amounting to 57 litres, which represented 54 kg. of the parings, was repeatedly cohobated in a current of steam until the odorous substances were finally contained in a volume of about 8 litres. The practically odourless liquids remaining in the large distilling flasks were mixed with those obtained by the cohobation of a larger quantity of the original distillate, and the whole examined as already described.

The above-mentioned concentrated distillate was extracted four times successively with specially purified ether, which was free from aldehyde. The united ethereal liquids were dried with anhydrous sodium sulphate, and the ether removed for the most part by distillation, after

which the liquid was brought into a small tared flask, and the remainder of the ether allowed to evaporate spontaneously. The amount of volatile product so obtained was 1.005 grms., thus representing 0.0035 per cent of the apple parings or about 0.0007 per cent of the entire fruit.

The essential oil was a yellow, somewhat viscous liquid, which gradually became darker on keeping, and possessed in a high degree the pleasant, characteristic odour of fresh apples. When cooled slightly below the ordinary room temperature it formed a soft, concrete mass, due to the separation of minute, acicular crystals, which evidently consisted of the previously mentioned paraffin hydrocarbon. A few drops of the oil, when shaken with a little water, gave all the above-noted reactions for acetaldehyde, and it also gave a decided reaction for furfural with aniline and hydrochloric acid.

The concentrated aqueous distillate which had been extracted with ether for the removal of the essential oil was made alkaline with sodium hydroxide and evaporated. It was then acidified with sulphuric acid and distilled in a current of steam. The faintly acid distillate was made alkaline with baryta, concentrated, and the excess of baryta removed by carbon dioxide. After filtration and concentration the liquid was found to contain an appreciable amount of formate, which was removed by oxidation with a 4 per cent solution of potassium permanganate in a current of carbon dioxide. The small amount of colourless solution eventually obtained gave on the addition of silver nitrate only a slight precipitate, which was too small for examination, but on concentrating the filtrate therefrom a very small amount of a silver salt was deposited, which was collected, washed with water, dried and analysed.

Subs., 0.0156: Ag, 0.0101.

Calc. for $\text{AgC}_2\text{H}_3\text{O}_2$: Ag, 64.6. Found: 64.7.

The distillate from which the essential oil had been removed was thus found to contain only formic and acetic acids.

PART II. Examination of Springdale Apples.

Occurrence of Traces of Methyl and Ethyl Alcohols.

It was noted in connection with the examination of Ben Davis apples that traces of methyl alcohol were found in the distillate. In order to confirm this observation it was deemed desirable to conduct a special experiment in which there could be no possibility of error, although the purified ether used for the previous extraction of the distillate had been carefully tested and found to be free from methyl alcohol. The variety of apples available for this purpose was that known as Springdale, and they were examined in the latter part of January.

A quantity of fresh parings from the apple, amounting to about 7.5 kg., was immediately distilled in large glass flasks by means of a current of steam, and about 5 litres of distillate were collected. The first portions of the distillate, which had a fragrant odour and contained some drops of oil, had a faintly acid reaction and responded to the tests for acetaldehyde. The entire amount of distilled liquid was repeatedly cohobated until the odorous or more volatile constituents were finally contained in a volume of

about 500 cc. To this liquid, contained in a flask provided with an inverted condenser, 10 grms. of sodium oxide hydroxide was added, and the mixture kept in active ebullition for two hours. It had then acquired a deep yellow colour with the separation of a small amount of aldehyde resin. After cooling, the alkaline mixture was distilled, and 20 cc. of distillate collected. This liquid, which had a pleasant odour, was saturated with common salt, and then extracted with light petroleum for the purpose of removing any higher alcohols. The salt solution was subsequently distilled, and this distillate subjected to further repeated distillations until finally 1.5 cc. was collected, the receiver being cooled with ice. A small portion (0.1 cc.) of this liquid when oxidised with potassium permanganate in strongly acid solution developed a distinct odour of formaldehyde, and when further treated according to the method of Denigès (*Loc. cit.*) a decided reaction for this aldehyde was obtained. As the last-mentioned substance was not contained in the original apple distillate, the presence of minute amounts of methyl alcohol was definitely established. It could naturally not be determined whether this alcohol was contained in the original distillate as such or in the form of an ester, and it may possibly have been produced during the distillation of the apple parings by the hydrolysis of a methyl ester of pectin (compare Tschirch, *Arch. Pharm.*, 1914, cclii., 538; von Fellenberg, *Biochem. Z.*, 1918, lxxxv., 45).

The remainder of the above-mentioned 1.5 cc. of concentrated distillate was tested for the presence of ethyl alcohol by means of the iodoform reaction, when distinct crystals of this substance were obtained.

The occurrence of ethyl alcohol in fruits and other parts of plants which have not undergone fermentation has previously been recorded by several observers (Lechartier and Bellamy, *Compt. rend.*, 1869, lxvix., 356, 466; Pasteur, *ibid.*, 1872, lxxv., 1054; Müntz, *ibid.*, 1878, lxxvi., 49; Berthelot, *ibid.*, 1899, cxxviii., 1366). Moreover, Gutzeit (*Ann.*, 1875, clxxvii., 344, 372, 382), by the distillation of several umbelliferous fruits, obtained both methyl and ethyl alcohols, which may have existed in the form of esters, and methyl alcohol or its esters was likewise found by Lieben in the products of distillation of meadow grass and leaves of trees (*Monatsh.*, 1898, xix., 333. Compare also Miller, Univ. Wisconsin, *Bull.*, 1919, cmxci.). It has, furthermore, been noted by A. Gautier (*Bull. soc. chim.*, 1876, xxv., 433) that he obtained 0.8 grms. of ethyl alcohol from 300 grms. of so-called *pommes gelées*, an expression which refers to a condition of some apples known as "water-core," but the fruit employed by us was of perfectly normal appearance.

Other Constituent of Springdale Apples.

All the aqueous liquids remaining from the concentration of the original distillate, together with the liquid remaining after the hydrolysis and distillation of the concentrated portion, were made alkaline with sodium hydroxide and evaporated to a small volume. The acids were then liberated by means of sulphuric acid and converted into barium salts in the manner previously described. As a considerable amount of formic acid was found to be present, this was first removed

by oxidation with potassium permanganate, and by subsequent precipitation with silver nitrate the following fractions of silver salt were obtained, the first of which became slightly reduced on drying.

- Fraction I. Subs., 0.0342 : Ag, 0.0168.
Found : Ag, 49.1.
Fraction II. Subs., 0.0245 : Ag, 0.0149.
Found : Ag, 60.8.
Fraction III. Subs., 0.0509 : Ag, 0.0317.
Found : Ag, 62.3.

These results indicated the acids to be chiefly formic and acetic, with a small amount of caproic acid.

On allowing the previously mentioned light petroleum extract to evaporate spontaneously in a suitable flask a very small amount of substance was obtained which possessed a pleasant odour. This was oxidised with 10 cc. of a chromic acid mixture and further treated in the manner previously described. The amount of barium salt eventually obtained was too small for analysis, but a portion of it on the addition of dil. sulphuric acid gave a pronounced odour of valeric acid, and the remainder when heated with absolute alcohol and a few drops of sulphuric acid developed the characteristic odour of ethyl valerate. There could thus be no doubt respecting the occurrence of amyl alcohol or its esters in Springdale apples.

PART III. Examination of Crab Apples.

As crab apples possess a particularly fragrant odour, and were available to us in considerable quantities, it was deemed of interest to compare their odorous constituents with those of the previously examined Ben Davis apple. The variety employed for this purpose consisted of the cultivated yellow fruit known as the "Golden Beauty."

The operations of paring the apples and conducting the distillation were precisely the same as those described in the first part of this paper. The amount of parings employed was 77 kg., which represented about 257 kg. of the entire fruit, and the total amount of distillate collected was 76 litres.

The distillate, which had a fragrant, apple-like odour, was somewhat opalescent, but on keeping for a few days the liquid became clear and an oily film separated on the surface. Even the first portions of the distillate were perfectly neutral to test-paper. It seemed desirable in this investigation to compare the yield and characters of the essential oil with those of the analogous product obtained from Ben Davis apples, and the total amount of distillate was, therefore, cohobated in a current of steam until the odorous constituents were concentrated in a volume of 10 litres. The first portions of this concentrated liquid were practically neutral and contained a considerable amount of acetaldehyde, but gave no reaction for furfural. On extracting the entire concentrated distillate with 4 successive portions of ether which was free from aldehyde, and removing the solvent, first by distillation and finally by spontaneous evaporation, there was obtained 3.3579 grms. of a pale yellow oil. This represented 0.0043 per cent of the apple parings or about 0.0013 per cent of the entire fruit.

The essential oil from crab apples possessed the same general character as that obtained from Ben

Davis apples, and no material difference in odour could be observed, although the yield of oil from the former was somewhat larger. The presence of both furfural and acetaldehyde was established by special tests.

After extracting the concentrated distillate with ether it was made alkaline with sodium hydroxide and distilled from a sand bath, the portion passing over below 97° being collected. This distillate consisted chiefly of ether with a small aqueous layer. After separating the latter and washing the ether several times with water the aqueous liquids were united, saturated with common salt, extracted with light petroleum (b.p. $30-55^{\circ}$), and distilled. On concentrating this distillate, and testing in the previously described manner the small portion which was first collected, a decided reaction for methyl alcohol was obtained. As the ether originally employed for extracting the aqueous distillate, when similarly tested, gave a perfectly negative result, the presence of minute amounts of methyl alcohol or its ester in the crab apple was definitely determined.

The above-mentioned aqueous, alkaline liquid, from which the portion boiling below 97° had been removed, was acidified with sulphuric acid and distilled in a current of steam until the distillate was practically neutral. The volatile acids were subsequently converted into barium salts, and as the latter were found to contain a considerable amount of formic acid, this was removed in the previously described manner by means of potassium permanganate. After finally concentrating the neutral solution it yielded with silver nitrate the following fractions of silver salt, which were analysed.

Fraction I. Subs., 0.0329 : Ag, 0.0208.

Fraction II. Subs., 0.0497 : Ag, 0.0317.

Fraction III. Subs., 0.0439 : Ag, 0.0282.

Calc. for $\text{AgC}_2\text{H}_3\text{O}_2$: Ag, 64.6.

Found: I., 63.2; II., 63.8; III., 64.2.

The concentrated distillate from crab apples, after extraction of the essential oil, was thus found to contain chiefly formic and acetic acids, with a very small proportion of an acid of higher molecular weight.

Examination of the Aqueous Liquids Remaining from the Cohobation of the Original Distillate. Identification of Formic, Acetic, and Caproic Acids.

The large amount of nearly odorless liquid remaining from the cohobation of 76 litres of the original crab apple distillate was made alkaline with sodium hydroxide and evaporated to a comparatively small bulk. It was then acidified with sulphuric acid, and subjected to distillation in a current of steam. The first portion of the distillate was strongly acid, had an odour of the higher fatty acids, and separated an oily film on the surface. After converting the entire amount of volatile acid into a barium salt, the latter was found to contain a considerable proportion of formate, and this was, therefore, removed by treatment with potassium permanganate in the manner previously described. The concentrated, neutral solution eventually obtained yielded with silver nitrate several successive fractions of silver salt, which were collected, dried, and analysed.

Fraction I. Subs., 0.0205 : Ag, 0.0099.

Fraction II. Subs., 0.0284 : Ag, 0.0138.

Fraction III. Subs., 0.0439 : Ag, 0.0215.

Calc. for $\text{AgC}_6\text{H}_{11}\text{O}_2$: Ag, 48.4.

Found: I., 48.3; II., 48.6; III., 48.9.

All the above fractions evidently consisted of nearly pure silver caproate.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxxi., No. 8.

COLLOIDAL SULPHUR.—M. Paul Barry.—It is possible to obtain sulphur suspensions of two distinct kinds, the first appears as a liquid with a milky appearance. The second variety is formed as a translucent liquid, colourless or faintly yellow when concentrated, by cooling, the liquid at first clear, afterwards has an appearance similar to the first type; the effect produced by lowering the temperature becomes more feeble as the solution is more concentrated. At a certain temperature, these liquids are absolutely stable, even to a concentration of 50 per cent. Colloidal sulphur is a body capable of absorbing water in fairly large quantities; this property is favoured by the presence of monovalent metallic salts such as hydrogen potassium, sodium in small quantities, whilst it is hindered by the presence of bivalent metallic salts (barium, magnesium, calcium, &c.) which coagulate the suspensions; coagulated sulphur does not absorb water; it is opaque and the granules are easily visible under the ultra-microscope, whereas in the stable suspensions of sulphur as in colloidal organic solutions, the granules are only just visible. Colloidal sulphur capable of furnishing aqueous solutions is not pure sulphur, but a mixture containing sulphur in a condensed state or strongly polymerised; these combinations of polymerised sulphur are easily dissociable and only stable in an aqueous medium in the presence of the elements which can stay the decomposition. Polythionic acids give translucent suspensions through the swelling of these bodies in water, similar to the action of gelatin, albuminoids, &c.; this swelling up is impeded or helped by the action of electrolytes. When the swelling becomes feeble, the granules lose their transparency, the liquid becomes milky, and it loses its stability. Polysulphuric acids and the polysulphides of the alkaline earths only swell feebly, and they only furnish unstable suspensions having a milky appearance.

NOTES.

POTASH DEPOSITS OF UPPER ALSACE.—These are said to underlie an area of more than 70 square miles, and to range from 6 to 30 feet in thickness. Estimates place the available quantity at more than 300,000,000 tons of K_2O . Now that the mines are under French control, considerable developments may be expected.

THE SIR JOHN CASS TECHNICAL INSTITUTE.—The new session of the Sir John Cass Technical Institute will commence on Monday, September 27. The courses of instruction provided are especially directed to the technical training of those engaged in Chemical, Metallurgical, and Electrical industries and in trades associated therewith. Full facilities are provided for those wishing to carry out work associated with the industries in which they are engaged or to undertake special investigation and research. The Chemistry, Metallurgy, and Physics laboratories are open both in the afternoons and evenings for work of this character. The instruction in experimental science also provides systematic courses in Chemistry, Physics, and in Pure and Applied Mathematics for the examinations of London University and in Chemistry and Metallurgy for the examinations of the Institute of Chemistry. Special courses of higher technological instruction form a distinctive feature of the work of the Institute. The curriculum in connection with the Fermentation Industries includes courses of instruction in "Brewing and Mating," "The History, Cultivation, and use of the Hop," and in the "Micro-biology of the Fermentation Industries." These courses are arranged for those engaged in the practical and scientific control of breweries, maltings, and other fermentation industries, who desire to acquire a knowledge of the technology and principles underlying their daily operations. A connected series of lectures on "Fuel and Power," comprising Liquid, Gaseous, and Solid Fuels and their application, Electrical Supply and Control, the Transmission of Power in Works, Fuel Analysis and Technical Gas Analysis, is also included in the syllabus of the Chemistry department for the forthcoming session. In the department of Physics and Mathematics, special courses of lectures will be given in "Colloids," the methods employed in their Investigation and their Relation to Technical Problems, in "Differential Equations and Vector Analysis," and in the "Theory and Application of Mathematical Statistics." In the Metallurgy department, in addition to courses of instruction in general Metallurgy, special courses of an advanced character are provided on Gold, Silver and Allied Metals, on Iron and Steel, on Metallography and Pyrometry, on the Heat Treatment of Metals and Alloys, on the Mechanical Testing of Metals and Alloys, and in Foundry Practice. These courses are designed to meet the requirements of those who wish to enter metallurgical industries or to qualify as assayers; also for those already engaged in industries associated with metals or mining and for those preparing for metallurgical or for prospecting work in the Colonies or abroad. Full details of the courses are given in the syllabus of the Institute, which can be had on application at the Office or by letter to the Principal. The Principal and Heads of the departments will attend at the Institute to interview students during the week Monday, September 20 to Friday, September 24, from 7 to 9 p.m.

BRITISH INDUSTRIES FAIR, 1921.—The White City, where the London section of the 1921 British Industries Fair is to be held, was opened jointly by King Edward VII. and M. Fallieres, President of the French Republic, on the occasion of the famous Franco-British Exhibition in May, 1908. The series of dual displays which followed

up to the outbreak of war in 1914 focussed the work, energy, and influence of those nations which were to become allies in the cause of humanity. The Franco-British Exhibition occupied a site of over 350 acres, not including the vast railway yards from which sidings were constructed throughout the grounds with services into the various buildings. The buildings and grounds represented a cost of ten million pounds, while the value of the contents amounted to one hundred million sterling. The total attendance during the months of May to October exceeded thirty millions. The sections were under the presidencies of various Ministers, the Rt. Hon. D. Lloyd George being President of the Engineering, Shipping and Manufacturers Section. In connection with the Exhibition was held the International Sports of the Olympic Games at the colossal Stadium inaugurated by King Edward VII. and attended by 150,000 spectators. The Imperial Exhibition, famous for the great Imperial Press Conference, followed in 1909, succeeded by the Japan-British Exhibition in 1910. The coronation of King George V. in 1911 was celebrated at the White City by a special Exhibition, in which the scenery and architecture of all parts of the Empire were reproduced, the native inhabitants occupying their respective sections and giving demonstrations of their handicrafts. The Latin-British Exhibition in the following year included Italy, Spain, Portugal, and the Latin countries of South America. The last of the series, the Anglo-American Exhibition, was held in 1914 to celebrate the centenary of peace between the English-speaking peoples. It continued until the outbreak of war, when the White City became a vast barrack, accommodating 16,000 of the troops recruited at the first call to arms. It is fitting, now that peace is again at hand, that the useful career of the White City should be continued by the British Industries Fair. The total capacity of all the buildings now available at the White City is thirty-five million cubic feet, giving a floor area exceeding 1,130,000 square feet, which should provide even for the requirements of the British Industries Fair. The Court of Honour and Arts, in which the Fair will be centralised, are admirably constructed for exhibition purposes. The former has a floor area of over one hundred thousand square feet, while the latter is eight hundred feet long and four hundred in width. The White City lies in the centre of a group of five railway stations, all with direct

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entrances to the exhibition buildings. Its means of transport are further augmented by various 'bus services from all parts of London, and an excellent tram service from the west and south. This makes it possible to reach the Fair from the "West End" of London in twenty minutes or half-an-hour. So numerous are the transport facilities that traffic of over one hundred thousand persons per hour can be handled, exclusive of taxis and private cars. At the same time the comparatively central position of the White City brings it within easy taxi distance of the West End hotels. In fact, from all points of view, situation, construction, transport, and general convenience the new site of the British Industries Fair leaves very little to be desired.

NOTICES.

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VOL. CXXI., No. 3154.

FUEL ECONOMY.* (Concluded from 139.)

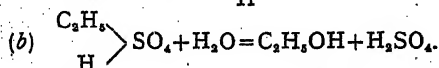
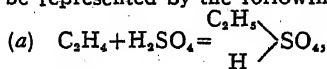
APPENDIX III.

Memorandum upon the Skinningrove Process for the Production of Alcohol from Coke Oven Gas.

The following is a brief outline of the process devised by Messrs. Bury and Ollander for the removal of ethylene from debenzolised coke oven gas and its conversion into ethyl alcohol.

The average amount of olefines present in a debenzolised gas from a typical Durham coking coal is usually between 2.0 and 2.5 per cent. They consist chiefly of ethylene with small quantities of propylene and possibly other higher members of the series.

The process for their removal from the gas is based upon the well-known fact that ethylene is absorbed by concentrated sulphuric acid forming ethyl hydrogen sulphate, which may be subsequently hydrolysed by the dilution of the acid with water yielding ethyl alcohol and sulphuric acid. The sequence of the reactions concerned may be represented by the following equations:—

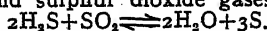


The problem presented to the investigators was not only the determination of the conditions under which 2 per cent of ethylene in an industrial gas can be rapidly absorbed by concentrated sulphuric acid so as to produce ethyl hydrogen sulphate exclusively, but also how the much smaller quantities of higher olefines contained in the gas can be removed from it prior to the desired absorption of ethylene.

Laboratory experiments proved (i.) that, although the absorption of ethylene by concentrated sulphuric acid proceeds far too slowly at ordinary temperatures, yet between 60° and 80° C., the time of contact required between the acid and coke oven gas, in order to ensure the absorption of 70 per cent of its total ethylene content, need be no more than 2½ minutes, and (ii.) that under such conditions the only product formed is ethyl hydrogen sulphate. On the other hand, if the temperature be allowed to exceed 80° C. some decomposition occurs and ethyl ether is produced.

The successful operation of such an absorption process on a large scale pre-supposes the elimination from the crude gas of tars, ammonia, naphthalene, and benzol hydrocarbons in the order named. At the Skinningrove Works the Otto direct process is employed for this purpose.

The next step consists in the successive elimination from the cooled and debenzolised gas of (a) sulphuretted hydrogen, and (b) higher olefines than ethylene, together with most of its water vapour content. For the elimination of the sulphuretted hydrogen it is proposed to make use of the well-known reaction between sulphuretted hydrogen and sulphur dioxide gases:—



The advantage of such a procedure is that it would not only dispense with the necessity of employing iron oxide purifiers (except perhaps as a final precaution), but it would also enable the small amount of sulphur dioxide arising from the reduction of the hot strong sulphuric acid during the later ethylene absorption process to be utilised.

Propylene and other higher olefines are next removed by scrubbing the gas with an 80 per cent sulphuric acid at the ordinary temperature in a tower on the counter-current principle, which also effects the removal of about 97 per cent of its water vapour content. The resulting cooled and dried gas is then passed through a "heat exchanger" situated so near the ovens that its temperature can be raised to between 60° and 80° C. at the expense of some of the sensible heat in the hot crude gas leaving the ovens. The strong acid (95 per cent) used for the absorption is also pre-heated to the same temperature. The scrubbing process for the removal of ethylene is carried out on the counter-current principle, and the time of contact between the pre-heated gas and acid is 2½ minutes, which is sufficient to effect absorption of 70 per cent of the total ethylene present. The acid can be used until it has absorbed up to 5 per cent of its weight of ethylene with the formation of a corresponding quantity of ethyl hydrogen sulphate.

The strong acid from the ethylene absorption towers containing the ethyl hydrogen sulphate is next taken to a special form of distilling column where it meets a current of steam which dilutes the acid to about 75 per cent strength and simultaneously hydrolyses the ethyl hydrogen sulphate forming ethyl alcohol and sulphuric acid. The heat produced during the dilution is sufficient to raise the temperature of the diluted acid to between 90° and 100° C., under which conditions the resulting alcohol distils over and is subsequently condensed, finally leaving the plant as a 95 per cent alcohol.

The diluted acid is finally pumped to the top of a Gaillard concentration tower where it is concentrated to a 95 per cent strength, which is then used over again for the absorption of ethylene. Any small quantity of sulphurous acid formed by the reducing action of the gases upon acids in the absorption tower is, during the dilution process, decomposed, and the resulting sulphur dioxide is (as aforesaid) utilised for the elimination of sulphuretted hydrogen from the debenzolised gas.

From figures given in Messrs. Bury and Ollander's paper (*loc. cit.*) the composition of the debenzolised gas from a Durham coking coal, before and after the removal of the greater parts of its ethylene content in the manner proposed, is as follows:—

	Before	After
Carbon Dioxide	2.0	2.08
Carbon Monoxide	5.4	5.61
Ethylene, &c.	2.0	0.62
Methane	25.0	25.96
Hydrogen	50.0	51.91
Nitrogen and Water Vapour, &c.	15.6	13.82

	Before	After
Gross	467.8	458.9
Net	412.2	402.8

W. A. BONE.

*Read before the British Association (Cardiff Meeting), Section B

APPENDIX II.

TABLE A.

Showing Tons of Coal exported from the United Kingdom in each of the years 1913 to 1919 inclusive, distinguishing the principal Countries to which consigned.

Countries to which consigned.	1913	1914	1915	1916	1917	1918	1919
Russia ...	5,998,434	3,087,805	42,559	4,804	1,075,005	128,114	221,490
Sweden ...	4,563,076	4,250,255	2,659,995	1,646,502	613,573	1,051,121	1,592,324
Norway ...	2,298,345	2,462,200	2,643,187	2,307,753	1,059,227	1,250,867	1,330,646
Denmark (including Faroe Islands)	3,034,240	3,059,162	3,130,642	2,305,409	856,037	1,045,701	1,742,711
Germany	8,952,328	5,256,765	—	—	—	—	4,301
Netherlands	2,018,401	1,722,215	1,792,951	1,346,129	376,819	88,001	401,901
Belgium ...	2,031,077	1,168,554	—	—	—	4,246	143,769
France ...	12,775,909	12,330,545	17,601,361	17,311,877	17,512,545	16,511,005	16,204,596
Algeria	1,281,664	910,211	939,846	721,803	616,053	160,340	523,091
Portugal ...	1,201,722	1,048,608	916,992	794,315	248,056	147,388	544,302
Azores ...	22,608	33,639	43,893	46,518	101,871	40,345	99,875
Madeira	131,751	87,378	61,870	46,139	25,024	6,367	29,749
Spain ...	2,534,131	2,260,362	1,597,083	2,007,899	773,030	429,003	805,740
Canary Islands	1,114,629	679,786	470,680	399,865	38,641	—	262,184
Italy ...	9,647,161	8,625,254	5,788,460	5,710,098	4,140,960	4,053,570	4,641,046
Austria-Hungary	1,056,634	564,362	—	—	—	—	142,567
Greece ...	727,899	578,757	309,198	168,106	18,540	41,328	139,315
Roumania	251,925	218,218	—	—	—	—	—
Turkey ...	369,789	429,506	10,324	5,987	40,513	19,136	135,738
Chile ...	588,526	377,482	46,407	24,194	13,154	9,000	7,204
Brazil ...	1,886,871	1,176,780	498,340	196,973	237,516	169,982	189,205
Uruguay ...	723,936	550,876	332,541	179,472	199,692	162,417	184,813
Argentine Republic	3,693,572	2,883,064	1,618,603	728,412	309,216	258,110	639,089
Other Foreign Countries	1,014,372	879,707	589,023	590,654	1,270,675	1,221,121	1,057,454
Total to Foreign Countries	67,919,000	54,641,491	41,093,955	36,542,909	29,526,147	26,797,162	31,043,200
Channel Islands ...	167,862	162,066	131,110	115,819	100,502	93,516	114,647
Gibraltar	354,702	309,650	356,075	517,135	1,224,340	1,615,985	1,465,736
Malta & Gozo	700,111	338,673	151,153	84,784	1,729,685	1,195,883	733,045
Egypt ...	3,162,477	2,594,723	1,362,073	844,398	1,574,251	1,697,908	1,675,163
Sierra Leone	40,602	35,524	23,492	12,186	226,648	160,899	48,333
Anglo-Egyptian Soudan	—	38,858	26,841	49,288	18,650	403	23,186
Aden and Dependencies	181,204	139,821	132,475	29,935	22,925	—	49,479
Ceylon and Dependencies	239,657	250,173	43,487	25,726	12,541	—	13,305
Hong Kong	52,408	10,376	—	—	—	—	12,241
Falkland Isles	27,977	34,678	67,432	50,416	29,840	24,344	34,490
Other British Possessions	554,118	483,847	146,467	78,957	530,258	166,804	36,743
Total to British Possessions	5,481,118	4,398,389	2,440,605	1,808,644	5,469,640	4,955,742	4,206,368
Total	73,400,118	59,039,880	43,534,560	38,351,553	34,995,787	31,752,904	35,249,568

TABLE B.

Showing Tons of Coal exported from each of the undermentioned districts of the United Kingdom during the years 1913 to 1919 inclusive.

	1913	1914	1915	1916	1917	1918	1919
Bristol Channel Ports	29,875,916	24,475,551	18,601,896	17,417,707	19,893,015	17,000,834	20,229,802
North - Western Ports	751,819	600,719	524,214	486,734	668,937	699,273	86,728
North - Eastern Ports	23,023,810	19,241,980	14,132,040	13,329,275	10,102,841	9,948,995	11,701,435
Humber Ports	8,883,353	6,049,741	3,791,392	1,804,953	1,812,724	1,617,719	530,471
Scottish Ports :							
East Coast	8,253,023	6,177,065	3,723,935	3,004,449	910,347	1,198,739	1,905,176
West Coast	2,184,174	2,201,244	2,724,005	2,297,088	1,564,291	1,212,692	745,899
Total (from Utd. Kgdm.	73,400,118	59,039,880	43,534,560	38,351,553	34,995,787	31,752,904	35,249,568

THE ODOROUS CONSTITUENTS OF APPLES. EMANATION OF ACETALDEHYDE FROM THE RIPE FRUIT.*

By FREDERICK B. POWER and VICTOR K. CHESNUT.

(Concluded from page 142).

By concentrating the filtrate and washings from the above-mentioned precipitates several additional fractions of silver salt were obtained.

Fraction.	Subs.	Ag. Found. G.	Per cent.
IV.	0.0353	0.0178	50.4
V.	0.1212	0.0616	50.8
VI.	0.0530	0.0273	51.5
VII.	0.0634	0.0329	51.9
VIII.	0.0805	0.0477	59.3
IX.	0.0724	0.0457	63.1
X.	0.0764	0.0487	63.7
XI.	0.0334	0.0215	64.4
Calc. for $\text{AgC}_2\text{H}_3\text{O}_2$: 64.6.			

In view of the composition of the first three fractions, and the gradual increase in percentage of silver, it may be considered that Fraction IV to X consisted of mixtures of silver caproate and acetate, especially as the last fraction was evidently nearly pure acetate. The rather close agreement of Fractions VI. and VII. with silver valerate, which requires 51.7 per cent Ag, is regarded merely as a coincidence, of the odour developed by all the salts on ignition was similar to that produced by caproic acid, and throughout the investigation there was otherwise no evidence of the presence of valeric acid.

The above results have thus shown the volatile acids of the crab apple to be the same as those of the Ben Davis apple, consisting chiefly of formic, acetic, and caproic acids, and, as will be indicated later, a very small amount of caprylic acid is also undoubtedly present.

Separation of the Aldehyde from the Distillate of Crab Apples, and its Further Identification as Acetaldehyde.

In the preceding examination of the apple distillates the presence of a notable quantity of acetaldehyde was observed, but its identification was effected only by the described qualitative tests,

which included, however, the characteristic reaction with dimethylamine and sodium nitroprusside. Inasmuch as the plan of the previously described investigation necessitated the treatment of the concentrated distillate with a caustic alkali, in order to effect the hydrolysis of the esters, and as this resulted in the destruction of the aldehyde, it was deemed desirable to conduct some special experiments whereby the identity of the aldehydic constituent could be further confirmed. It was also considered important to ascertain that the acetaldehyde was not accompanied by a higher homolog, since some of these compounds possess highly odorous properties, and incidentally the alcoholic constituent of the crab apple esters has also been determined.

For the above-mentioned purpose 17.24 kg. of fresh crab apple parings were brought immediately into a still, and the material subjected to distillation in a current of steam. The first portion of the distillate, being concentrated, was set aside, and the distillation then continued so long as any odorous substances passed over. The weaker distillate was subsequently concentrated by repeated cohobation, until finally the concentrated distillate amounted to about 500 cc. This liquid was saturated with sodium hydrogen sulphite, and the mixture set aside for several days, after which it was extracted five times successively with pure, aldehyde-free ether. The examination of these ethereal liquids will subsequently be described. The sulphite solution was made alkaline with sodium carbonate and distilled in a current of steam until about 500 cc. of distillate was obtained. The first portion of the distillate possessed an odour which was chiefly that of acetaldehyde, but also reminding somewhat of a higher aldehyde, and the total distillate was slightly opalescent. It yielded in a high degree all the previously described aldehyde reactions, including that characteristic of acetaldehyde. A special test for formaldehyde with phenylhydrazine hydrochloride gave a perfectly negative result, thus confirming the previous observations regarding the absence of this compound in the apple distillate.

The distillate containing the aldehyde was treated with an alkaline solution of potassium permanganate until the red colour was permanent, after which it was filtered, the excess of permanganate removed by the addition of a solution of

* From *Journal of the American Chemical Society*, July, 1920.

ferrous sulphate in dil. sulphuric acid, and the mixture distilled in steam. The entire acid distillate, which had a very slight odour, was made alkaline with barium hydroxide, and the liquid filtered and concentrated. On the subsequent addition of a few drops of solution of silver nitrate a slight blackish precipitate was produced, which was removed by filtration, after which by fractional precipitation a series of perfectly white silver salts was obtained. These were dried over sulphuric acid and analysed.

Fraction.	Subs. G.	Ag. Found. G.	Per cent.
I.	0.0486	0.0311	64.0
II.	0.0374	0.0240	64.2
III.	0.0558	0.0359	64.3
IV.	0.0485	0.0312	64.3
V.	0.0822	0.0527	64.1

Calc. for $\text{AgC}_2\text{H}_3\text{O}_2$: 64.6.

These results indicate that the aldehyde obtained from the crab apple was nearly pure acetaldehyde, with possibly a trace of a higher homolog.

The total amount of silver salt obtained was 0.6493 grms., which would correspond to 0.1711 grms. of acetaldehyde, or about 0.001 per cent of the weight of apple parings employed. Inasmuch as the yield of essential oil, which naturally would contain but little of the aldehyde, was 0.0043 per cent, the proportion of the latter in the original apple distillate was relatively large.

Hydrolysis of the Esters. Identification of Amyl Alcohol.

As previously mentioned, the concentrated crab apple distillate after saturation with sodium sulphite was extracted several times with ether in order to remove the non-aldehydic substances. The united ethereal liquids, which gave no reaction for aldehyde, were washed with a little water, dried with anhydrous sodium sulphate, and the greater part of the ether removed by distillation. The liquid was then brought into a small tared flask, and the remainder of the ether allowed to evaporate spontaneously, when there was obtained 0.2677 grms. of a yellowish oil which had an intense, and, when diluted, pleasant apple-like odour. This represented 0.0015 per cent of the weight of the apple parings. The oily product was mixed with 200 cc. of water, 10 grms. of sodium hydroxide added, and the mixture heated for two hours in a flask provided with an inverted condenser. It was then allowed to cool and distilled in a current of steam. The first portion of the distillate separated some oily drops and had the odour of amyl alcohol. The entire distillate was extracted five times with pure, aldehyde-free ether, the united ethereal liquids dried with anhydrous sodium sulphate, and the greater part of the ether removed by distillation, the remainder being then allowed to evaporate spontaneously in a flask provided with a glass stopper. To this residue, consisting of a few drops of yellowish oily liquid, 10 cc. of the previously mentioned chromic acid mixture was added, and the whole heated on a water-bath, with occasional agitation, for about 15 minutes. It was then cooled, diluted with water, and extracted five times with pure ether. The united ethereal liquids were washed with a little water, and then extracted four times successively with a 5 per cent solution of barium hydroxide in portions of

25 cc. each. These alkaline liquids were saturated with carbon dioxide to remove the excess of baryta, and the filtered solution concentrated. On the subsequent addition of silver nitrate a very small amount of a nearly white precipitate was obtained, which was collected, washed with a little water and dried.

Subs., 0.0196: Ag, 0.0100.

Calc. for $\text{AgC}_5\text{H}_9\text{O}_2$: Ag, 51.7. Found: 51.0.

This result showed that the salt was silver valerate, it afforded evidence that the crab apple, like ordinary apples, contains amyl alcohol in the form of esters.

No further amount of silver salt could be obtained from the above-mentioned solution, but the evaporated mother-liquor on the addition of dil. sulphuric acid developed the odour of valeric acid. The ethereal liquid from which the valeric acid had been extracted by means of baryta was washed with water, dried with anhydrous sodium sulphate, and the ether removed, but it yielded a scarcely perceptible residue.

Acids obtained by the Hydrolysis of the Esters.

The strongly alkaline liquid remaining after the hydrolysis of the esters and subsequent distillation was acidified with sulphuric acid and again distilled in a current of steam. The first portion of distillate was opalescent, and a very small amount of solid substance separated in the condenser, but it was gradually carried over and probably consisted of caprylic acid, which melts at 16.5° . The entire amount of volatile acid so obtained was converted into a barium salt, and the concentration solution of the latter yielded with silver nitrate a perfectly white silver salt, which was analysed.

Subs., 0.0975: Ag, 0.0459.

Calc. for $\text{AgC}_8\text{H}_{17}\text{O}_2$: Ag, 48.4.

Calc. for $\text{AgC}_9\text{H}_{19}\text{O}_2$: Ag, 43.0. Found: 47.1.

This result indicated the salt to consist of a mixture of silver caproate and caprylate, the former largely predominating.

Acids Remaining in the Original Distillate after Cohobation.

The large volume of aqueous liquid remaining from the concentration of the original distillate by cohobation was made alkaline with sodium hydroxide and evaporated. It was then acidified with sulphuric acid and distilled in a current of steam, the volatile acids being subsequently converted into a barium salt. As the solution of the latter was found to contain a considerable amount of formic acid, this was removed by means of potassium permanganate in the manner previously described. The filtered and concentrated neutral liquid eventually obtained gave with silver nitrate a small precipitate, which was collected, dried, and analysed.

Fraction I. Subs., 0.0450: Ag, 0.0224.

Found: Ag, 49.8.

This salt evidently consisted chiefly of silver caproate, which requires 48.4 per cent Ag, together with a little acetate. By the evaporation of the mother-liquor two other portions of salt were successively obtained and analysed.

Fraction II. Subs., 0.0635: Ag, 0.0384.

Fraction III. Subs., 0.0510: Ag, 0.0328.

Calc. for $\text{AgC}_2\text{H}_3\text{O}_2$: Ag, 64.6.

Found: I., 60.5; II., 63.6.

From the above results it may be concluded that the aqueous liquid remaining after cohobation of the original distillate contained chiefly formic and acetic acids with a small proportion of caproic acid.

PART IV. *Emanation of Acetaldehyde from Ripe Apples.*

The occurrence of acetaldehyde among the products of distillation of odorous substances has frequently been observed in recent years and it has indeed been stated (Gildemeister and Hoffmann, "Die aetherischen Oele," second edition, Bd. II., p. 480) that it is probably never entirely absent in any essential oil, although on account of its ready solubility in water, as well as its great volatility, it is mostly contained in the water of the distillate from which the oil has been separated. It has, however, hitherto been assumed that the lower aliphatic aldehydes are first produced in the process of distillation and that they do not exist as such in the plant (*Ibid.*, Bd. I., p. 422). Semmler has particularly noted (Semmler, "Die aetherischen Oele," 1906, Bd. I., p. 568) that from the standpoint of vegetable physiology acetaldehyde would gain in importance if it could be proved that it occurs ready formed in the plant. Inasmuch as the present authors had found that considerable amounts of acetaldehyde are contained in the distillate from ripe apples, it was deemed of special interest to ascertain whether this compound could be detected in the odorous emanation from the fruit, and the experiments in this direction have been completely successful.

In the month of December a quantity of sound red apples of the variety known as "Nero" was brought into a large copper vessel, provided with a tightly-fitting cover and a small opening both at the top and the bottom, so that a current of air could be slowly aspirated through it. In this experiment 215 apples were used, which weighed 31.85 kg. The air which entered the vessel at the top was first passed through an alkaline solution of potassium permanganate and then through conc. sulphuric acid. At the bottom the exit tube was first connected with a small inclined glass apparatus consisting of a series of bulbs and containing a saturated solution of sodium hydrogen sulphite. To this bulb apparatus an empty gas-washing bottle was attached and to the latter a similar bottle containing a saturated solution of sodium hydrogen sulphite, the whole being then connected through an intervening empty flask with a filter pump, by means of which the air was continuously drawn through the entire system. This operation was allowed to proceed uninterruptedly for seven or eight days, when the absorbing apparatus was detached, and the liquid through which the air had passed was then found to possess a pleasant apple-like odour. The entire amount of sulphite solution contained in the bulb apparatus and gas-washing bottle was about 300 cc. It was made alkaline with sodium carbonate and distilled, the first distillate of about 50 cc. being then again distilled and 5 cc. of liquid collected, the receptacle having been cooled with ice. The concentrated distillate so obtained had the characteristic odour of acetaldehyde, immediately reduced an ammoniacal solution of silver oxide in the cold, and gave within a few seconds a deep pink colouration with Schiff's reagent. It also gave with dimethylamine and sodium

nitroprusside the deep indigo-blue colour which is characteristic of acetaldehyde. (As several works of reference designate the use of trimethylamine in the specific test for acetaldehyde, the fact may again be noted that the reaction is not obtained with this reagent, unless it may by chance contain some dimethylamine).

The above-described operation was subsequently conducted with several other varieties of apples, which were loosely packed in a large conical glass percolator, but otherwise the conditions were the same.

The second experiment was made early in January, and 60 "Paragon" apples were used, which weighed 9.37 kg. For the third experiment, begun in the middle of January, a green variety of apple known as the "Keeper" was employed, and 57 of them weighed 9.18 kg. A final experiment was made early in February with crab apples, which were of the same kind and quality as those used for the previously described chemical examination of this fruit. This variety of apple being small in size the number used was 150, which weighed 9.6 kg.

In all the above-mentioned experiments the aldehyde was liberated from its bisulphite compound, and in the subsequent tests for its identification the same decisive results were always obtained. The interesting fact has thus been established that the odorous emanations from the apple during its period of vital activity contain acetaldehyde, and it follows that the occurrence of this compound in a distillate from the fruit does not depend upon any chemical changes in the process of distillation.

Summary.

The results of the present investigation, for which several varieties of apples were employed, may be briefly summarised as follows.

1. The odorous constituents of apples have been found to consist essentially of the amyl esters of formic, acetic, and caproic acids, with a very small amount of the caprylic ester and a considerable proportion of acetaldehyde. In considering the relative amounts of the respective alcohol and acids it seems probable that the latter are also present to some extent in the free state.

2. It has been shown that acetaldehyde is a product of the vital activities of the fruit, and that it occurs in the exhalations of ripe apples. This observation is deemed of considerable biological importance, especially as it has hitherto been assumed that the lower aliphatic aldehydes are first formed during the process of steam distillation. It is, for example, quite probable that the exhalation of acetaldehyde may prove to be one of the factors involved in the production of so-called "apple-scald," an affection to which some apples are subject when stored without free circulation of air (compare Brooks, Cooley and Fisher, *J. Agr. Res.*, 1919, xviii., 211-240).

3. The aqueous distillate from fresh apple parings has been found to contain, in addition to the above-mentioned substances, exceedingly small amounts of methyl and ethyl alcohols and also a small amount of furfural. Inasmuch as the last compound is doubtless produced by chemical changes in the material during its distillation, it can not be regarded as one of the odorous constituents of the apple.

4. The essential oil, as extracted by means of ether from a concentrated distillate of either ordinary apple parings or those of the crab apple, is at ordinary temperatures a yellowish, somewhat viscid liquid, becoming much darker on keeping. When slightly cooled it forms a concrete mass, due to the separation of small acicular crystals, which consist of a paraffin hydro-carbon. It possesses in a high degree the characteristic, fragrant odour of fresh apples. Besides the esters mentioned, it has been found to contain, by specific test, small amounts of acetaldehyde and fural. The yield of oil from the parings of the Ben Davis apple was 0.0035 per cent, and that from the more odorous crab apple 0.0043 per cent, which corresponds to about 0.0007 and 0.0013 per cent respectively of the entire ripe fruit.

5. Although amyl valerate is generally designated in chemical literature as "apple oil," it is quite certain that this compound has never been identified as a constituent of apples, and in the course of this investigation no evidence could be obtained of its presence. On the other hand it has been shown that the characteristic, fragrant odour of ripe apples is due to a mixture of the previously enumerated substances, which may exist in varying proportions in the numerous varieties of the fruit, thus giving rise to slight differences of odour.

AGGREGATION AT THE MELTING POINT

By WILLIAM R. FIELDING, M.A., M.Sc. (Vict.),
Senior Science Master at King Edward VII. School, Lytham.

(Continued from p. 88).

TABLE IX. shows the observed and the calculated atomic heats of different blocks of elements. The former are mostly between 273° and 373° , and the latter at the melting points. It will be noticed that the observed atomic heats (with several exceptions) fall as the melting points rise, whereas the calculated atomic heats naturally rise.

TABLE IX.

	Block of elements.	Average At. Ht.	Temp. of Obs.	Calc. At. Ht.	Average M.P.
I.	He to Cl (2° - 171°) 10 elements	—	—	4.67	70°
II.	Hg to Li (234° - 459°) 12 elements	6.40	190°-400°	6.48	341°
III.	Se to Al (490° - 932°) 12 elements	6.33	273°-450°	6.71	700°
IV.	Ra to Cu (973°-1356°) 12 elements	6.12	273°-450°	6.88	1172°
V.	Mn to Zr (1503°-1973°) 12 elements	5.97	273°-450°	7.03	1729°
VI.	Nb to C (1973°-3873°) 16 elements	5.60	273°-373°	7.74	2556°

Table X shows the values of the theoretical specific heats arranged according to the periodic classification.

TABLE X.

[illegible]

Observations.

1. Several elements are polymerised at the M.P.; e.g., Be, B, C, N, O, etc., each polymer acting, as regards specific heat and M.P., as if it were an element whose atomic weight were p times the real atomic weight (where p =degree of polymerisation). All elements with abnormally low specific heats are polymerised. In these cases the highest observed specific heats are less than the calculated values.

2. Elements like Ni, whose observed specific heats are greater than the calculated, are beginning to break up, even at the M.P., into "molecules" of half the usual size. E.g., the atomic heat of nickel is doubled between 100° and 400° so that from the latter temperature to the M.P., 1725°, it is not improbable that it is present as Ni₂ and Ni₃, where the average element is present as M_{2n}.

3. In each group of elements (with occasional exceptions) and very often in each series, the specific heat falls with increase of atomic weight.

4. Without exception the Argon elements have the lowest calculated specific heats in their series and these values are considerably less than the corresponding values of the first members in the next higher series. This phenomenon may be due to the fact that these elements are monatomic (or M_n and not M_{2n}) in the solid state, so that their observed specific heats will be double the calculated specific heats and the family, instead of following the halogens (so that all non-metals are together), should precede Group I., and form the left-hand part, perhaps, of the Iron Group (Group VIII.). In Table X, both sets of values for the Argon elements are given.

Specific Heats of Compounds.

It is generally agreed that the investigations of Joule, Kopp, Tilden, &c., have established the fact that the molecular heat of a compound is additive; i.e., it is the sum of the atomic heats of the constituent elements, and from this generalisation the atomic heats of chlorine, fluorine, hydrogen, oxygen, &c., were calculated in the "solid" state. The results of Tilden (Table XI.), who showed that the sum of the atomic heats of tellurium and nickel at different temperatures, is equal to the molecular heat of nickel telluride at the same temperature, certainly cannot be lightly set on one side.

TABLE XI.

Absolute Temperatures	Atomic Heats Ni	Atomic Heats Te	Sum	Observed Molecular Heat of Nickel Telluride
100	3.5	5.85	9.20	8.38
200	5.12	5.06	11.08	11.35
300	6.14	6.08	12.22	12.41
400	6.81	6.19	13.00	12.92
500	7.19	6.30	13.49	13.15
600	7.43	6.42	13.85	13.28
700	7.58	6.53	14.11	13.35

It is assumed that the nickel and tellurium are both present in the "solid" state, just as water of crystallisation is present in the "solid" state; but if it is agreed that the only difference between solids, liquids, and gases is in their degrees of aggregation, then it is difficult to see how the same degree of aggregation, or even average aggregation, exists in a compound as in the constituent elements. A silver molecule contains about 19

silver atoms, an iodine molecule about five iodine atoms, and, as will be shown later, a silver iodide molecule 5.8 molecules. Therefore, 110 atoms of silver (5.8 molecules) and 110 atoms of iodine (22 molecules) yield 110 molecules of silver iodide (only 19 molecules); i.e., 27.8 molecules of silver and iodine yield only 19 molecules of silver iodide. It is almost certain, then, that the mean distance between two consecutive silver atoms in a silver molecule is not the same as the mean distance between two silver atoms in a silver iodide molecule. Moreover, the silver aggregation in free silver is a 19 aggregation but the silver aggregation in silver iodide is a 5.8 aggregation. Therefore silver, even in solid silver iodide, cannot be present in the solid state. In fact, the only thing solid about silver iodide is the silver iodide itself, and neither of its component parts. We will now proceed to apply our formula—

$$r = \frac{4.15 \times R}{\text{M.P.}}$$

to compounds and the reader is asked to remember that in the case of compounds:—

(1) R refers to the total numbers of atoms in the molecules of any particular compound.

(2) The molecular weights corresponding to any M.P. are obtained from Table VIII. by interpolation, if necessary.

(3) In Table XII, the observed results are generally given at the "ordinary" temperatures, whereas my calculated specific heats are always at the melting point. In some cases the agreement is very close but the reader must be prepared for even great differences (see the rapid changes in the specific heats of nickel, tellurium, and nickel telluride with rise of temperature—Table XI.).

TABLE XII.

Compounds	M.P.	Melt. Wts.	R (No. of Atoms in molecule)	Spec. Heat Obs.	Heat Calc.	Calculated Molecular Ht.
KCl	1063	1780	48	0.173	0.187	13.9
KBr	1023	1657+	28	0.107	0.113	13.45
KI	978	1640	19.8	0.0819	0.0838	13.9
NaCl	1088	1810	61.9	0.214	0.236	13.8
NaBr	1038	1710	33.2	0.137	0.133	13.7
NaI	923	1555	20.7	0.0881	0.093	13.95
AgCl	733	1182	16.5	0.091	0.0928	13.32
AgBr	699	1120	12	0.074	0.0709	13.32
AgI	829	1362.7	11.6	0.061	0.0577	13.56
CaCl ₂	1053	1765	48	—	0.189	20.98
CaBr	1038	1725	26.64	—	0.1065	21.3
CaI ₂	1013	1710	17.25	—	0.0706	20.76
BaCl ₂	1233	2037	29.31	0.090	0.099	20.59
SrCl ₂	1146	1890	36	0.120	0.121	19.19
CaCl ₂	1053	—	—	—	—	—
PbCl ₂	758	1230	13.2	0.066	0.0722	20.08
HgI ₂	526	844	5.6	0.0423	0.044	—
Hg ₂ I ₂	563	890	5.44	0.0395	0.0401	—
ZnCl ₂	373	600	13.2	0.136	0.147	20
AlCl ₃	467	745	22.3	—	0.2	26.7
AlBr ₃	363	590	8.8	—	0.1	26.7
AlI ₃	458	735	7.2	—	0.0652	26.6
K ₂ SO ₄	1323	2020	81.2	0.196	0.254	44.2
ZnCl ₂	373	600	13.2	0.136	0.147	20
ZnBr ₂	667	1052	14	—	0.087	19.6
ZnI ₂	719	1158	10.86	—	0.0626	20

TABLE XIII.

Compound.	M.P.	Melt. Wt.	R	s	Mol. Heat	Mol. Heat of Water
Na ₂ SO ₄	1136	1880	92.5	0.338	48	—
Na ₂ SO ₄ .10H ₂ O	305.5	471	54	0.735	236.55	18.85
NaOH	583	939	70.5	0.502	20.08	—
NaOH.H ₂ O	337	530	55	0.677	39.27	19.19
NaOH.2H ₂ O	285	430	50.76	0.739	56.16	18.04
Zn(NO ₃) ₂ .3H ₂ O	318.5	496	36.54	0.48	116.8	—
Zn(NO ₃) ₂ .6H ₂ O	309.4	477	43.2	0.58	172.5	18.56
P ₂ O ₅	296	450	20.5	0.287	31.57	—
(H ₃ PO ₃) ₂	343	544	46.2	0.559	91.68	20.11
SO ₂	288	437	21.84	0.315	25.2	—
H ₂ SO ₄	283.5	428	30.66	0.448	43.9	18.7
H ₂ SO ₄ .4H ₂ O	248	375	41.8	0.7	119	18.8

(4) The observed specific heats quoted in this paper have been selected from standard textbooks—Roscoe and Schorlemmer's "Chemistry," Watson's "Physics," Scott's "Introduction to Chemical Theory," Lothar Meyer's "Outlines of Theoretical Chemistry," and *Physikalisch-Chemische Tabellen* von Landolt und Börnstein.

Water supplies us with very interesting results. Melting at 273°, it has a melticular weight of 412 and R is 69. On substituting in

$$\frac{\text{M.P.} \times S}{R} = 4.15$$

s works out at 1.048, nearly twice the observed value. Tilden found the specific heat of ice between 195° and 273° to be 0.47 and Person obtained the value 0.504. "It is now generally recognised that water in the liquid state consists of at least three kinds of molecules, monohydrol (H₂O), dihydrol (H₂O₂), and trihydrol (H₂O)₃, in different proportions in equilibrium with one another. The relative amounts of the three kinds vary with the temperature, the monohydrol increasing with rising temperature at the expense of the trihydrol. (Ice consists practically entirely of trihydrol: steam of monohydrol)." See *Science Progress*, No. 53, p. 32).

In the equation

$$s = \frac{4.15 \times R}{\text{M.P.}}$$

if M.P. is fixed, then the only way to halve s is to halve R (or the number of atoms in the water molecule). If R is halved, then the melticular weight will be halved and this value would correspond to a lower melting point. The same difficulty was met with in the case of carbon, silicon, &c., whose calculated specific heats were considerably greater than the highest observed results. How can we explain these exceptions to what seems a general law? Only by a wide recognition of the principle of polymerisation. In the water melticle we found 69 atoms and a melticular weight of 412. To retain this melticular weight and yet have only half the number of atoms we must regard two water molecules to become one, forming one "heavy" molecule of water whose "molecular" weight is 36. This view is in keeping with the known behaviour of water in the solid state when it is almost entirely trihydrol.

Where the calculated specific heat at the melting point is greater than the observed specific heat it points to some degree of polymerisation. For instance, the atomic heat of diamond is 0.76 at 223°, 1.35 at 283°, and 5.5 (the highest value)

at 1258°, while the calculated atomic heat at its M.P. is about 9.29, or nearly twice the highest observed value. The carbon molecule appears to be C₂ at its M.P. and perhaps C₁₄ or C₁₂ at 223°; from 1258° to its M.P. it remains C₂, but at, say, 358° when its atomic heat is 2.12 its molecule is C₂ or a mixture of C₄ and C₆.

The highest observed atomic heat of graphite is 5.5 at 1251°, pointing to C₂ between that temperature and its melting point; but it is only 1.37 at 223° from which it appears that the graphite molecule at this temperature is C₆.

The case of nickel has already been referred to.

Combined Water.

Owing to the exigency of space the author will bring this paper to a close by calculating the molecular heat of combined water. The molecular heat of ice is about 9 but the value for water, between 273° and 373°, is about 18.

In no case, I believe, has the specific heat of any of the above solid substances been found and so it is difficult to say whether the water present is present as trihydrol (H₂O)₃ or monohydrol (H₂O). But using Kopp's atomic heats for hydrogen (2.3), oxygen (4), nitrogen (5.3), it appears that when water is present in a compound, p is often less than 2; i.e., the water is not all in the "solid" state. See Table XIV.

TABLE XIV.

Compound	Calculated Molecular Heat.	Probable Molecular Heat.	p.
Na ₂ SO ₄	48	34	1.41
Na ₂ SO ₄ .10H ₂ O	236.55	120	1.97
NaOH	20.08	12.9	1.55
NaOH.H ₂ O	39.27	21.5	1.83
NaOH.2H ₂ O	56.16	30.1	1.87
Zn(NO ₃) ₂ .3H ₂ O	116.8	67	1.74
Zn(NO ₃) ₂ .6H ₂ O	172.5	92.8	1.86
P ₂ O ₅	31.57	24.8	1.27
(H ₃ PO ₃) ₂	91.68	50.6	1.81
SO ₂	25.2	18.8	1.34
H ₂ SO ₄	43.9	27.4	1.60
H ₂ SO ₄ .4H ₂ O	119	61.8	1.92
H ₂ SO ₄	43.9	27.4	1.60
KHSO ₄	46.38	31.3	1.48
K ₂ SO ₄	(48)	34	1.41
Na	—	—	1+
NaOH	—	—	1.55
HOH	—	—	2
SO ₂	—	—	1.34
H ₂ O.SO ₂	—	—	1.60
H ₂ O	—	—	2

Thus, it seems clear that the more combined water is present, the nearer does the value of ϕ approach 2; i.e., the mere H_2O is present in the solid state.

Table XV. gives the value of ϕ for the compounds mentioned in Table XII.

TABLE XV.

	P.		P.		P.
KCl	1.08	NaCl	1.11	AgCl	1.04
KBr	1.00	NaBr	1—	AgBr	1—
KI	1.02	NaI	1.05	AgI	1—
CaCl ₂	?	HgI ₂	1.04	PbCl ₂	1.09
BaCl ₂	1.1	Hg ₂ Cl ₂	1.01		
SrCl ₂	1.008	ZnCl ₂	1.08		
Na ₂ SO ₄	1.41				
K ₂ SO ₄	1.41				

Knowing ϕ for certain compounds, it is not difficult to calculate the molecular heat of the common radicles, and, within certain limits, the specific heat and melting point of any substance.

(To be continued.)

MINERAL RESOURCES OF THE WORLD.

Felspar.

THE Imperial Mineral Resources Bureau have issued a pamphlet of sixteen pages of statistical and technical information relative to the production and consumption of felspar in the British Empire and foreign countries during the war period, 1913-1919.

Felspars are complex silicates of aluminium and other metals, and they are divided into three divisions from the commercial standpoint:—

1. Potash felspar, including orthoclase and microcline, containing potash as well as alumina;
2. Albite, containing soda and alumina;
3. Soda-lime felspars, notably oligoclase and labradorite, containing a mixture of soda and lime as well as alumina.

Representative analysis of these different kinds of felspars are given showing their composition.

	Orthoclase	Albite	Oligoclase	Labradorite
Silica ...	65.72	68.46	62.30	52.55
Alumina ...	18.57	19.31	22.00	28.32
Ferric Oxide ...	—	0.28	0.04	2.44
Potash ...	14.02	—	0.94	0.64
Soda ...	1.25	11.27	8.20	4.52
Lime ...	0.34	0.68	4.86	11.61
Magnesia ...	0.10	—	—	0.48
Totals	100.00	100.00	98.34	100.56

The felspar used for industrial purposes is mostly quarried as orthoclase or microcline, and the

report mentions that if the deposit is to be worked at a profit, the deposit should have a thickness of at least 25 feet and should be free from deleterious minerals such as mica, garnet, tourmaline, hornblende, apatite, and pyrites.

Its uses are included in the manufacture of glass, particularly chemical ware; as a body and glaze in china and pottery; in the manufacture of artificial teeth; as a flux in the manufacture of emery and carborundum wheels; and the waste impure felspar is ground up for use as a poultry grit and roofing spar.

The report gives a review of a new process for the extraction of alumina from labradorite which has recently been introduced in Norway.

"In this process the felspar is leached with a 30 per cent solution of nitric acid whereby the aluminium, calcium, and part of the iron are converted into nitrates, the balance of the iron and the whole of the silica remaining undissolved. After removing the iron, the solution is evaporated to dryness, and the residue heated to such a temperature that the aluminium salt only is decomposed. The nitrogen oxides driven off during ignition are collected in the form of nitric acid. It is proposed to use the sodium nitrate and calcium nitrate by-products as fertilizers, and the alumina for the manufacture of aluminium or aluminium salts."

The production of felspar throughout the world is next discussed, each country being taken separately; the United States of America, the chief producer of felspar, consumes its own output in addition to the high-grade felspar produced in Canada. A table is given showing the output of felspar in the different countries between the years 1913 and 1919.

PROCEEDINGS OF SOCIETIES.

INSTITUTE OF METALS.

Annual Meeting, September 15, 1920.

THROUGH the courtesy of the Secretary of the Institute of Metals we are able to publish the following abstracts of the papers read at the Meeting of the Institute on September 15. It may be possible in the near future to reproduce some of these very important communications in full.

"Brass Foundry Practice at Messrs. Vickers, Limited, Barrow-in-Furness." By H. B. WEEKS, F.I.C., Member (Barrow-in-Furness).

In these notes Mr. Weeks describes the brass foundry and the progress that has been made

World's Production of Felspar.

	(In Metric Tons.)						
	1913	1914	1915	1916	1917	1918	1919
United Kingdom ...	67,714	61,694	49,970	37,473	33,708	37,603	48,651
Canada ...	15,236	16,388	13,211	17,684	17,661	17,044	—
Australia ...	—	—	—	—	47	—	—
Germany (Bavaria) ...	—	3,105	1,970	2,650	2,530	—	—
Italy ...	—	700	700	900	1,292	1,517	—
Norway (exports) ...	40,842	27,967	12,607	12,811	4,435	—	—
Sweden ...	37,878	20,818	12,105	12,724	18,533	17,850	—
United States ...	100,760	122,885	95,388	120,400	128,788	89,670	—

therein during the last 50 years. He deals with loose pattern moulding, plate moulding, "dry" and "green sand" work, loam moulding, chill moulding, and the dressing and fettling, including sand-blasting. Reference is also made to the premium bonus system which is in operation.

He stated that one of the most predominant factors in the successful working of the foundry is probably the system adopted for metal control, and makes reference to the means which are in operation in order to keep the various alloys to their proper composition. The foundry equipment is also described, including electric and hydraulic cranes, drying stoves, melting plant, riddles and sand mixers, portable mould dryers, ladles, ash washing and the briquetting of scrap by hydraulic pressure.

The metallurgical side is under scientific control and experimental work has been the means of developing a number of alloys that have found useful application throughout the services. The total output of castings from the brass foundry during the five years covering the war period was nearly 17,000 tons.

The Note should prove of special interest and service to those who are chiefly interested in practical brass foundry work.

"Crystal Growth and Recrystallisation in Metals." By Prof. H. C. H. CARPENTER, M.A., Ph.D., A.R.S.M., F.R.S., Member (London), and CONSTANCE F. ELAM, Member (New Barnet).

The research is divided into two main parts. In the first the authors describe their observations on the growth of crystals in an alloy of tin and antimony containing 1.5 per cent of the latter metal, which is well adapted for studying this phenomenon. It is shown that in all the cases studied, growth took place by "boundary migration," and not by coalescence; that large crystals can grow at the expense of small ones and vice versa; that orientation does not influence growth and that a crystal can grow and be grown into at the same time.

In the second part of the paper, so far as can be judged from the experiments made to test the question, the crystals of castings do not grow provided care is taken to prevent deformation. The authors' results indicate that work followed by heat is the real cause of crystal growth. The conditions under which very large crystals are formed have been carefully studied and defined. The crystallisation is always observed to take place in the boundaries of the old crystals. No existing theory of crystal growth explains the new facts described in the paper. These theories are discussed by the authors.

"The Influence of Gases on High-Grade Brass." By T. G. BAMFORD, M.Sc., Member (Birmingham), and W. E. BALLARD, Member (Birmingham).

When melting brass in ordinary fuel furnaces the metal comes into contact with divers gases, and their effect on the metal and the quality of the castings have been studied by the authors.

The tendency of gases towards absorption was determined by gradually heating a small sample of brass in a comparatively large volume of each gas and noting pressure changes. The rate of chemical reaction was measured by maintaining constant gaseous pressure above a sample for a

considerable time at selected temperatures and measuring directly the volume of gas absorbed. An entirely new apparatus was designed with which to study the solubility of gases in brass. The novel feature was that determinations were made at atmospheric pressure. External variations of pressure during any experiment was guarded against by means of a compensating bulb.

Large scale casting experiments were carried out to determine under what thermal conditions of casting the porosity due to gases could be eliminated.

Briefly summarised, the results of the experiments have established the following facts. Sulphur dioxide reacts with high grade brass at all temperatures between 700° C. and 1100° C. at atmospheric pressure. The rate of reaction is rapid between 800° C. and 1100° C., but above this temperature there appears to be a reversal. Hydrogen is soluble in 70:30 brass in large quantities, the quantity absorbed increases steadily with rise in temperature, and large quantities of the gas may be removed by heating the solid metal in such gases as carbon dioxide or air. Hydrogen dissolves in zinc in small quantities, and the solubility decreases with the rise of temperatures.

Provided the pouring temperature is maintained as high as 200° C. above the liquidus porosity due to gases is absent. A higher temperature is needed for tube casting than for solid billets of similar weight. Incidentally it was shown that where unsoundness exists it is more generally confined to the top of the casting, and further as a comparative test it is immaterial in which part of a tube or billet a test piece is taken provided a uniform system is adopted throughout.

"The Constitution of the Alloys of Aluminium and Magnesium." By D. HANSON, M.Sc., Member (Teddington), and MARIE L. V. GAYLER, B.Sc., Member (Teddington).

This paper describes the results of an investigation into the aluminium series of alloys. The equilibrium diagram given by Grube, which previously has been the only one available, was incomplete. The work of the authors shows that it needs considerable revision, and they have now worked out the complete constitution over the whole system of alloys.

It is shown that aluminium and magnesium form two compounds with each other. One has the formula Al_2Mg_3 (37 per cent magnesium). It has a melting point of 450° C. at which temperature there is a maximum on the liquidus curve. It forms a eutectic with aluminium, containing 33 per cent magnesium, the freezing point of which is 477° C. Aluminium can dissolve Al_2Mg_3 to give a solid solution containing up to 11 per cent magnesium consist of homogeneous solid solution.

The second compound probably has the composition Al_2Mg_3 (57 per cent Mg). It forms eutectics with both Al_2Mg_3 and magnesium. The Al_2Mg_3 - Al_2Mg_3 eutectic contains about 41 per cent magnesium and melts at 446° C. Al_2Mg_3 will dissolve Al_2Mg_3 and Mg in appreciable quantities, and alloys containing from 47 to 60 per cent magnesium consist of homogeneous solid solutions. The eutectic of Al_2Mg_3 and magnesium contains about 70 per cent magnesium and melts at 436° C. Al_2Mg_3 is soluble in magnesium. The saturated solution at 420° C. contains about 10

per cent aluminium and at 150° C. about 9 per cent aluminium.

The solubility relationships of all the constituents in the solid alloys have been determined by annealing samples of the alloys for long periods, followed by quenching and examining them under the microscope. The solidus has also been determined in the same manner.

"The Effect of Increasing Proportions of Antimony and Arsenic Respectively upon the Properties of Admiralty Gun-Metal." By R. T. ROLFE, F.I.C., Member (Bedford).

In this research two series of synthetic alloys were prepared showing, in one series, a progressive increase in antimony up to 1.5 per cent, and in the other series, in arsenic up to 1 per cent, both sand- and chill-castings being made, while casting temperatures were determined and complete analyses made of all the different compositions. Each alloy was later re-melted, and a second series of sand- and chill-castings obtained, of which again analyses were made, casting temperatures determined, and mechanical tests carried out. The following are the conclusions:—

Antimony.—In sand-cast gun-metal, this impurity progressively increases the hardness and decreases the strength and ductility. If a proportion of about 0.75 per cent is exceeded, the minimum specification figures for tensile strength and elongation may not be reached. Chill castings show the same tendency in a modified degree. Antimony has no effect on the soundness of the castings except in the case of chill-cast metal melted twice, when with increasing antimony is associated increasing unsoundness. To avoid this a figure of 0.75 per cent must not be exceeded. No effect on the microstructures can be observed.

Arsenic.—In sand-cast metal melted once, increasing arsenic causes a falling-off in both strength and ductility. A maximum figure of 0.3 per cent is suggested. In re-melted metal and in chill castings this effect of arsenic is rather masked. Arsenic has no effect on soundness except in the case of chill-cast metal melted twice, when increasing arsenic is associated with increasing unsoundness. A maximum figure of 0.4 per cent is suggested. Arsenic has no influence on the hardness. The arsenic figure influences the microstructures in sand castings but not in chill-castings.

"The Constitution and Structure of Certain Tin-Antimony-Copper Alloys." By O. F. HUDSON, D.Sc., Member (London), and J. H. DARLEY, Member (London).

The work of the authors had for its immediate object a study of bearing metals of a particular composition (tin 89 per cent, antimony 8.7 per cent, and copper 2.3 per cent), principally with a view to ascertaining if any rules could be formulated connecting easily recognised variations in structure with definite casting conditions. Before proceeding to a detailed examination—photomicrographic and otherwise—of the complicated tin-antimony-copper bearing metals, the authors deal in their paper with the two binary systems, tin-copper and tin-antimony, since the ternary alloys are most conveniently considered as a simple combination of alloys of the binary systems of corresponding composition. In other words, the constituents of the binary alloys appear practically unchanged in composition and properties in

the ternary alloys, the characteristic structure in the white metals being due rather to the special arrangements of these constituents than to the appearance of any new phase.

The authors consider that the essential condition for the production of a coarse angular type of structure in bearing alloys is undisturbed cooling from a particular temperature, and that the casting temperature of a white metal bearing should not exceed this critical temperature. Near the critical temperature the structure appears sensitive to differences in the rate of cooling (temperature of mould and size of casting), but above or below this temperature the type of structure is unaffected by comparatively wide variations in the rate of cooling. The critical temperature will depend on the composition of the alloy and in the case of the alloy used in these experiments it lies between 300° and 350° C. In other alloys in which solidification begins at higher or lower temperatures the critical temperature will be correspondingly higher or lower, but generally the angular type of structure will result when the casting temperature is about 50° C. above the temperature at which the alloy begins to solidify.

In conclusion, the authors desire to express their thanks to the Admiralty for permission to publish this paper.

(To be continued).

NOTES.

BRITISH INDUSTRIES FAIR.—Prospectuses have been issued by the Board of Trade in connection with the Glasgow Section of British Industries Fair, which will take place in the Kelvin Hall, Kelvingrove, from February 28 to March 11, 1921. The classification of exhibits for the fair are textiles (woollens, cotton, silk, linen, jute, &c.), boots, shoes, slippers, and leggings, chemicals (light and heavy), dyes, domestic chemical products, foodstuffs (prepared and preserved), and cardboard boxes (as used in all trades represented at the Fair. The Glasgow Corporation, under the auspices of, and with the support of the Board of Trade, are organising the Fair and there is every prospect that the coming show will be more successful than any of its predecessors. An extensive scheme of advertising in the Press of the colonies and friendly foreign countries has been decided upon, as a result of which the attendance of overseas buyers at the different Fairs (London, Glasgow, and Birmingham) will be more numerous than ever. In addition the Board of Trade (Department of Overseas Trade) have sent out information about the Fairs, and issued invitations to buyers all over the world through Consuls and Trade Commissioners. A spacious building specially erected for exhibition purposes by the Glasgow Corporation will house the Fair. Following the success of the show held in February of this year, the hall has been extended, and it is now the largest building exclusively used for exhibitions in Great Britain. Enquiries regarding the Fair should be addressed to Mr. James M. Freer, Kelvin Hall of Industries, Kelvingrove, Glasgow.

A CORRESPONDENT wishes to know where he can obtain spanish wax of the kind used to seal the stems of flowers for preservation.

THE COAL FIRE.—H.M. Stationery Office have published for the Department of Scientific and Industrial Research a report entitled "The Coal Fire," which describes the work carried out by Dr. Margaret Fishenden in connection with a research into Domestic Heating; the investigation was directed by the Air Pollution Advisory Board of the Manchester City Council, and grants-in-aid of the work have been made by the Research Department. The investigation into the efficiency of open fires has yielded a collection of carefully ascertained data from which it is believed that a new departure can be made in dealing with the whole question of the use of coke and other forms of smokeless solid fuel in domestic fires. The work is of so important a character that it has been arranged, in consultation with the Manchester Air Pollution Board, that the report should be published; it is hoped that in this way the work will receive the wide publicity it deserves. Copies price 4s. (by post 4s. 3d.) may be obtained through any bookseller or directly from H.M. Stationery Office, at the following addresses: Imperial House, Kingsway, London, W.C.2; 28, Abingdon Street, London, S.W.1; 37, Peter Street, Manchester.

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3155.

THE CONSTITUTION AND STRUCTURE OF THE CHEMICAL ELEMENTS.

By HAWKSWORTH COLLINS.

THE NUMBER 23.

THE following investigation chiefly concerns the heavier elements as the simpler elements from H to Mn were considered in the CHEMICAL NEWS, December 26, 1919.

Since it has been proved: (1) that the atomic weights are integers (CHEMICAL NEWS, November 28, 1919), *i.e.*, that all the elements are polymers of hydrogen; (2) that the atomic weights of triads are even integers, and those of perissads odd integers, of which the only exception so far found is nitrogen (CHEMICAL NEWS, December 19, 1919); (3) that there are in general large errors in the higher atomic weights (CHEMICAL NEWS, November 28, 1919); (4) that the higher the atomic weight the greater is the probable error (CHEMICAL NEWS, November 28, 1919); (5) that when oxygen is taken as 16 the errors in general make the atomic weights too large, and when H is taken as the unit the errors make the atomic weights too small (CHEMICAL NEWS, April 9, 1920); it is evident that the experimental atomic weights referred to H as unit are as important as those calculated from $O=16$ also that the integers indicated by these five proofs are not obtained arbitrarily for each one is the nearest odd or even integer to the two experimental atomic weights according as the element has odd or even maximum valency. These integers are given in Table I.

TABLE I.

	Integers	At. wts. $O=16$	At. wts. $H=1$
Fe	56	55.84	55.44
Co	59	58.97	58.53
Ni	59	58.68	58.28
Cu	63	63.57	63.1
Ga	69	70.1	69.6
Ge	72	72.5	71.9
As	75	74.96	74.4
Se	78	79.2	78.6
Br	79	79.92	79.32
Kr	82	82.92	82.3
Rb	85	85.45	84.75
Sr	88	87.63	86.97
Yt	89	89.33	88.63
Zr	90	90.6	89.9
Mo	96	96.0	95.3
Ru	101	101.7	100.9
Rh	102	102.9	102.1
Ag	107	107.88	107.12
In	115	114.8	113.9
Sn	118	118.7	117.8
Sb	119	120.2	119.3
I	127	126.92	125.85
Te	128	127.5	126.5
Xe	130	130.2	129.2
Ba	136	137.37	136.36
La	139	139.0	138.0

	Integers	At. wts. $O=16$	At. wts. $H=1$
Ce	140	140.25	139.25
W	184	184.0	182.6
Os	191	190.9	189.5
Ir	192	193.1	191.6
Pt	194	195.2	193.7
Au	197	197.2	195.7
Hg	199	200.6	199.1
Tl	204	204.0	202.5
Pb	206	207.2	205.65
Nt	222	222.4	220.6
Ra	226	226.0	224.0
Th	232	232.15	230.3
U	238	238.2	236.4
Zn	66	65.37	64.9
Cd	112	112.40	111.6
Cb	93	93.1	92.4
Pd	106	106.7	105.9
Cs	133	132.81	131.8
Ta	181	181.5	180.1
Bi	207	208.0	206.4

Cu is known to act either as a monad or as a dyad, and it is generally supposed that the monadic valence is one of the two dyadic valences, but it will be shown later that this is not the case; so that Cu is really a triad and must be represented by an odd integer. The same remarks also apply to Hg.

Of the 83 recognised elements, the first 25 in ascending order of atomic weight have already been considered, and 12 are rare elements about which little is known and which cannot be arranged satisfactorily in the Periodic Table. The remaining 46 are given in Table I., so that there is no arbitrary choice of elements.

In Table II., a very large generalisation is given connecting the integers in Table I., supported by four sets of coincidences.

TABLE II.

	Na	Na	At. wt. divided into
Mg ^{II}	Na - H		2 portions
Al ^{III}	Na - H - H ₃		3.....
Si ^{IV}	Na - H - H ₃ - H		4.....
P ^V	Na - H - H ₃ - H - H ₃		5.....
S ^{VI}	Na - H - H ₃ - H - H ₃ - H		6.....
Cl ^{VII}	Na - H - H ₃ - H - H ₃ - H - H ₃		7.....
Cr ^{VI}	Na - H - Na - H - H ₃		5.....
Mn ^{VII}	Na - H - Na - H - H ₃ - H		6.....
Cu ^{II}	Na ₁ - Ca ^{II}	63 = 23 + 40	
Ga ^{III}	Na ₃	69 = 3 × 23	
Se ^{VI}	Na ₂ - S ^{VI}	78 = 2 × 23 + 32	
Rb ^I	Na ₂ - K ^I	85 = 2 × 23 + 39	
Zr ^{IV}	Na ₂ - Sc ^{IV}	90 = 2 × 23 + 44	
Mo ^{VI}	Na ₃ - Al ^{III}	96 = 3 × 23 + 27	
Ru ^{VII}	Na ₂ - Mn ^{VII}	101 = 2 × 23 + 55	
Rh ^{VI}	Na ₂ - Fe ^{VI}	102 = 2 × 23 + 56	
Cd ^{II}	Na ₂ - Zn ^{II}	112 = 2 × 23 + 66	
In ^{III}	Na ₂ - Ca ^{III}	115 = 2 × 23 + 69	
Sn ^{IV}	Na ₂ - Ge ^{IV}	118 = 2 × 23 + 72	
Iv ^I	Na ₄ - Cl ^{IV}	127 = 4 × 23 + 35	
Ba ^{II} or iv	Na ₂ - Zr ^{IV}	136 = 2 × 23 + 90	
Ce ^{even}	Na ₄ - Ti ^{even}	140 = 4 × 23 + 48	
Hg ^{odd}	Na ₄ - Ag ^{odd}	199 = 4 × 23 + 107	
Nt ^o	Na ₄ - Xe ^o	222 = 4 × 23 + 130	
Th ^{iv}	Na ₄ - Ce ^{iv}	232 = 4 × 23 + 140	
U ^{even}	Na ₂ - Ir ^{even}	238 = 2 × 23 + 192	
Ra ^{II}	Na ₆ - Sr ^{II}	226 = 6 × 23 + 88	
Pt ^{even}	Na ₄ - R ^{even}	194 = 4 × 23 + 102	

The four coincidences in Table II. are:—

1. Of all the elements Na is the most likely one to enter into the constitution of several elements, as it is more widely distributed than any other.

2. Table II. connects pairs of elements, which are already known to be similar chemically, or which are especially associated with one another in mineralogy. (The latter data will be given in the next paper).

3. The number of portions (Na) added to the one of any pair in order to form the other is always such that the valency of the heavier can be explained. *E.g.*, suppose that Zn and an element similar to it chemically had been found to have a difference of 23 in their atomic weights, it would have been impossible to explain how they could both be dyads, knowing that the electric charges are quiescent in pairs; but since $\text{Cd} = \text{Na}_2\text{Zn}$, it is evident that if the pair of valences emanating from Na, are quiescent, Cd would have the same valency as Zn.

4. The following facts, which concern a large proportion of the elements given in Table II., show that there is frequently present in the constitution of the heavier element of a pair something which is common to them all and which causes each heavier element to be more volatile than the lighter element, or which causes the former to melt or volatilise at an abnormally low temperature:—

(a) K melts at 335° abs. temperature, Rb (Na_2K) at 311° , Cs (Na_2K) at 300° .

(b) Zn melts at 692° , and Cd (Na_2Zn) at 594° .

(c) Ag melts at 1234° , and Hg (Na_2Ag) at 234° .

(d) I (Na_2I) easily volatilises.

(e) Na melts at 368° , and Ga (Na_2) at 303° .

The latter liquifies between the fingers, and cryolite (Na_3AlF_6) melts in a candle-flame.

(f) Ge melts at about 1173° , and Sn (Na_2Ge) at 605° .

(g) In (Na_2Ga) melts at 449° , an abnormally low temperature.

(h) Ce melts at a lower temperature than either Cb or Ti.

(i) Ba melts at a lower temperature than Zr. The following fact is important in this connection:—All alloys except Na_2K and NaK , are solid at the ordinary temperature.

The number 23 occurs 70 times in connection with the 41 elements concerned in Table II. 23 is a large number under the circumstances. It would have been a very awkward matter for demonstration if the main constituent of the elements had been represented by a small number, say, 5, for instance; but, being as large as 23 the matter becomes very apparent, and the probability of its truth is very much greater than it would otherwise be.

Although one or two of the results of Table II. may in the future be shown to be wrong, it is quite impossible that such a large generalisation as this could be evolved if there were no truth in it.

Remarks by the International Committee with regard to this year's list of atomic weights make it plain that chemists admit that large errors have not yet been eliminated. In the case of boron they say that Smith and Van Haagen find that its atomic weight is 10.9 instead of 11, and that they discuss all previous determinations and show

wherein they were affected by errors. The reduction of 11 to 10.9 is equivalent to a reduction of 1.0 in Cd which would bring it down from 112.4 to 111.4, or to a reduction of nearly 2.0 in the case of Pb. Again, with regard to Zr the International Committee say that Venable and Bell by pointing out sources of error in all previous values find its atomic weight to be 91.76 (not yet authorised) instead of 90.6.

Even if these two proposed alterations are found in the future to be incorrect, still the two admissions with regard to errors hold good.

It is not intended to be inferred that the heavier element has always been actually formed by the union of the lighter element with one or more masses of 23, but that there is a difference in their constitutions of one or more such masses. Some of the cases to which this remark specially refers are Zr, Sn, Ba, and Nt. *E.g.*, it is not intended to be inferred that Sn has been formed by the union of Na, with Ge, because Sn is never found associated with Ge in minerals, but that the combination of Na_2Ge is due to the inter-relationship of the elements.

If the nearest integer for Cb had been 94 instead of 93 it would have come into the generalisation as Na_2Ti ; and if the nearest odd integer for Cs had been 131 instead of 133 it would have come in as Na_2Rb or Na_2K . Evidence that the actual atomic weights of Cb and Cs are 94 and 131 will be given when each element is considered separately.

The following facts (Tables III. and IV.) could not be brought into Table II. (except those in brackets) because the pairs of elements are not obviously connected either in chemistry or mineralogy, but they are connected by the inter-relationship of the elements.

TABLE III.

Mg ^{II}	24	H ^I	1	Yt ^{III}	89	Zn ^{II}	66
Al ^{III}	27	He ^{II}	4	Ru ^{VII}	101	Se ^{VI}	78
Cu ^{III}	63	Ca ^{II}	40	Rh ^{VI}	102	Br ^{VII}	79
K ^I	39	Os ^{II}	16	Cd ^{II}	112	Yt ^{III}	89
V ^V	51	Si ^{IV}	28	Sb ^V	119	Mo ^{VI}	96
Mn ^{VII}	55	S ^{VI}	32	Xe ⁰	130	Ag ^I	107
As ^V	75	Cr ^{VI}	52	Tl ^{IV}	204	Ta ^V	181
Se ^{VI}	78	Mn ^{VII}	55	Bi ^V	207	W ^{VI}	184
Br ^{VII}	79	Fe ^{VI}	56				

In each of these 17 pairs of elements there is a difference of 23 in the atomic weights, and at the same time a difference of one valence. Considering any one of the pairs, *e.g.*, As and Cr, it is evident that if a mass of 23 with one valence were added to a mass of 52 with six valences, and if two of the seven became quiescent, (the result would be a mass of 75 with five valences. Similar remarks apply to all the other 16 pairs.

TABLE IV.

Mo ^{VI}	96	Al ^{III}	27	Te ^{VI}	128	Co ^{III}	59
Se ^{VI}	78	Gl ^{III}	9	Ta ^V	181	Cd ^{II}	112
Yt ^{III}	89	Ne ⁰	20	W ^{VI}	184	In ^{III}	115
Cb ^V	93	Mg ^{II}	24	Hg ^{III}	199	Xe ⁰	130
Te ^{VI}	128	Ni ^{II}	59				

In each of the nine pairs of elements in Table IV. there is a difference of 69 ($=3 \times 23$) in the atomic weights, and also a difference of +3 in the valences.

The number 23 has now been shown to connect 58 elements out of a total of 71, so that the matter is far removed from any possibility of chance, not

merely because there are so many differences of 23, but because *the addition of a mass of 23 always corresponds with the gain or loss of one valence.*
Proof that the above generalisations are not due to chance.

Table III. gives all the cases in which an addition of a mass of 23 to an element produces an element whose valency is either one greater or one less than that of the lighter element; but in order to prove that the state of affairs is not due to chance it is necessary to consider all the pairs of elements whose masses differ by 23, whether the results are favourable or unfavourable. So in addition to the data given in Table III. the following must be considered:—S (32) ... Cl (55), Cl (35) ... C (12), Kr (82) ... Co (59), Kr (82) ... Ni (59), Nt (222) ... Hg (199).

(a) There are now altogether 22 pairs of elements, each pair differing by a mass of 23. The probability that the difference of the valences of any pair would accidentally be ± 1 is $1:2$, (where $+1$ means that the larger of the pair has one more valence than the other, and -1 means that the lighter has one more valence than the other). *E.g.*, if the valency of the lighter mass were 2, the valency of the heavier might be 1, 3, 5, or 7; or, if the valency of the lighter were 3, that of the heavier might be 0, 2, 4, or 6. Therefore the probability that 17 out of 22 would accidentally have a difference in their valences of ± 1 in preference to the other two possibilities is $1:2^{22}-3^{22}=1:2^{12}=1:4096$.

(b) There are ten pairs of elements, given in Table II., with a difference of 46 ($=2 \times 23$) in their atomic weights, and no difference in their valences. Five other pairs have a difference in their valences, viz., Mn (55) ... Cl (9), Zn (66) ... Ne (20), Ga (69) ... Na (23), Te (128) ... Kr (82), La (139) ... Cb (93). The probability that any pair would accidentally have no difference in its valences is $1:4$. *E.g.*, if the valency of the lighter element had been 4, the heavier might have been 0, 2, 4, or 6; and if the valency of the lighter had been 5 the heavier might have been 1, 3, 5, or 7. Therefore the probability that 10 pairs out of 15 would accidentally have no difference in their valences is $1:4^{15}-5^{15}=1:48$.

(c) There are nine pairs given in Table IV. with a difference of 69 ($=3 \times 23$) in their atomic weights, and with a difference of $+3$ in their valences. There are four other pairs which do not conform to this general rule with regard to their valences, viz., Rb (85) ... O (16), Sr (88) ... F (19), Ru (101) ... S (32), Hg (199) ... Xe (130). The probability that any pair would accidentally have a difference of $+3$ in its valences is $1:4$. *E.g.*, if the valency of the lighter element were 3, that of the heavier might be 0, 2, 4, or 6. Therefore the probability that 9 pairs out of 13 would accidentally have a difference of $+3$ in their valences is $1:4^{13}-4^{13}=1:47$.

(d) Therefore the probability that all three coincidences have happened together by accident is $1:2^{12}+16+14=1:2^{42}$ —one to four billion.

(a) proves that it is not a matter of chance that an additional mass of 23 generally produces a gain or loss of one valence; (b) proves that there is no accident in the observation that an additional mass of 46 generally produces no change in the valency (the pair being quiescent); (c) proves that there is no accident in the observation that an

additional mass of 69 generally produces a gain of three valences; and the three proofs together (d) make it infinitely probable, *i.e.*, certain that a mass of 23, from which emanates one valence, takes a prominent part in the formation of the elements.

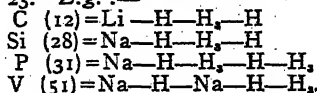
As some may think that this proof is vitiated by the fact that the nearest odd or even integers are employed instead of the actual experimental atomic weights ($0=16$), the matter may be considered in the following way.

When the experimental atomic weights as given at present are employed, the approximate number 23 occurs 100 times in Tables II., III., and IV., and in 90 of these it lies between 22.5 and 23.5, and in 50 it lies between 22.9 and 23.1, and it is much more extraordinary that one valence can be shown to emanate 100 times from a mass which is always approximately 23 than that one valence can be shown to emanate 100 times from a mass which is always exactly 23.

When a state of affairs has been proved to be due to cause and not to chance it is evident that no future discoveries or additions to knowledge (such as isotopes, *e.g.*) can ever contradict the general truth obtained, for it is impossible for scientists to unconsciously evolve a state of affairs which can be proved to be due to cause and not to chance, and yet for it not to contain an absolutely incontrovertible truth.

Table II. explains why the principle of the inter-relationship of the elements does not always apply equally well to the heavier elements as it does to the simpler ones. The chief reasons are, first, that more than two of the simpler elements come into the constitution of the heavier ones; secondly, that there are no elements of masses 46 ($=2 \times 23$) and 92 ($=4 \times 23$).

The only numbers which have previously been observed to connect similar elements are 16 and 20; but both these are chiefly due to the number 23 as shown in the CHEMICAL NEWS, December 26, 1919; for the 16 is explained by the replacement of a 7 by a 23, and the 20 is due to replacement of a 3 by a 23. *E.g.*—



A NEW THEORY RELATING CONSTITUTION TO TASTE.* (PRELIMINARY PAPER).

SIMPLE RELATIONS BETWEEN THE CONSTITUTION OF
ALIPHATIC COMPOUNDS AND THEIR SWEET TASTE.

By ERNEST OERTLY and ROLLIN G. MYERS.

Introduction.

THE relation between the constitution of substances and their taste has always been of interest to the chemist and the physiologist. It has been well known for a long time that most of the acids taste sour. Previous to the advent of the dissociation theory this fact was hardly associated with the presence of any one element or group. It is now pretty certain that the hydrogen ions are the

* From the *Journal of the American Chemical Society*, xli., No. 6, June, 1919.

essential constituent. At least they alone are common to all the acids possessing this quality. The ionic theory may account for the "salty taste" of sodium chloride, sodium sulphate, and other sodium salts in a similar way. The peculiar taste of typically basic substances such as potassium hydroxide and sodium carbonate, is associated with the presence of the common hydroxyl ion. In view of these facts and inferences it was logical to extend the analysis to organic compounds and to try to discover the particular atoms or groups common to substances having a sweet or bitter taste.

It has been pointed out by Nef that most of the compounds corresponding to the formula $(\text{CH}_2\text{O})_n$ are sweet. Through the work of Emil Fischer ("Untersuchungen über Aminosäuren," etc., 1906) we became acquainted with the fact that many of the α -amino acids have a sweet taste. L. Henry (*Compt. rend.*, 1895, cxxi., 213) sought to connect the taste of certain bitter compounds with the group $-\text{CNO}_2\text{CH}_2\text{OH}$. Finally, G. Cohn ("Die Organischen Geschmackstoffe," 1914) in his remarkable study of organic tastestuffs compiled an enormous amount of evidence, which proved that there is a close relation between constitution and taste. His work confirmed Henry's theory which he amplified by showing that taste in general is dependent on the presence of certain groups, such as the hydroxyl and amino groups. He calls them sapophoric groups. He points out that those sapophoric groups occur frequently in pairs. Finally, he cites a great number of instances showing that the lower members of certain homologous series have a sweet taste, while the higher members of the same series may be tasteless or bitter. He fails, however, to supply us with a simple theory which could include these facts and which would permit chemists to classify tastestuffs. And we still lack simple rules by which it would be possible to predict the taste of a given compound by a simple inspection of its formula.

Mode of Procedure.

We decided to start our investigation with the sweet aliphatic compounds. They are, of all the tastestuffs, undoubtedly the most important, both from a chemical and physiological point of view. A great number of facts are known in connection with this subject. The relations within each class (sugars, amino-acids, halogen compounds) are pretty well known, while the lack of a theory embracing all the more important among them has been felt most keenly.

In approaching this problem we took advantage of the experience of other chemists who had attempted and finally succeeded in finding a relation between constitution and the dyeing properties of organic compounds. This relationship, as is well known, has been satisfactorily explained by O. N. Witt (*Ber.*, 1876, ix., 522) and others by attributing these properties to two different kinds of groups, the so-called chromophoric groups, that are characterised by a double bond, and the auxochromic groups. A substance containing a chromophoric group is called a chromogene. A chromogene is a coloured substance, a potential dyestuff, so to speak, yet it is only by the introduction of one or several auxochromic groups that those compounds are transformed into real dyestuffs. We shall see that something similar holds true for the constitution of tastestuffs.

The Glucophores of Aliphatic Compounds.

As has been pointed out repeatedly by Cohn (*Loc. cit.*, p. 118), the sweet taste of organic compounds is frequently bound to one or two sapophoric groups, which very often occur in pairs. This observation we considered to be a good starting point, but it had to be extended.

Instead of attributing the sweet taste of a given compound to one factor, the glucogene (Cohn) or glucophore, as we prefer to call it, we maintain that it is due to two distinct factors, a glucophore and an auxogluc.

Any glucophore will form a sweet compound with any auxogluc. It is the purpose of the present study to determine just what aliphatic groups may act as glucophores, and which as auxoglucs.

Definition.—We define the glucophore as a group of atoms which has the power to form sweet compounds by uniting with a number of otherwise tasteless atoms or radicals.

A preliminary examination of the literature revealed the existence of the following glucophores:—

1. $\text{CH}_2\text{OH}.\text{CHOH}$ —Glycol, $\text{CH}_2\text{OH}.\text{CH}_2\text{OH}$, which is the most simple substance in which this glucophore occurs, may be considered as a combination of the group $-\text{CH}_2\text{OH}.\text{CHOH}$ —and hydrogen. Glycol is sweet, as A. Wurtz pointed out many years ago.

If the same glucophore, $\text{CH}_2\text{OH}.\text{CHOH}$ —, is linked to the methyl radical or ethyl radical, we obtain 1,2-propanediol $\text{CH}_3.\text{CHOH}.\text{CH}_2\text{OH}$, and 1,2-butanediol $\text{CH}_3\text{CH}_2.\text{CHOH}.\text{CH}_2\text{OH}$, respectively, two other sweet compounds.

If we combine this glucophore with the methylol-radical, CH_2OH —, then we get glycerin, which is notoriously sweet.

The group $\text{CH}_2\text{OH}.\text{CHOH}$ — falls clearly within our definition.

2. $-\text{CO}.\text{CHOH}$ —(H). This second glucophore yields with two hydrogen atoms glycolaldehyde, the simplest sugar.

With the methylol radical CH_2OH —, the glucophore $-\text{CO}.\text{CHOH}$ —(H), yields two different compounds. If the radical $-\text{CH}_2\text{OH}$ is linked to the carbinol of the glucophore, and the hydrogen atom H is bound to the carbonyl group of the glucophore, we obtain the glyceric aldehyde $\text{CH}_2\text{OH}.\text{CHOH}.\text{CHO}$.

If furthermore the methylol radical is linked to the carbonyl of the glucophore, while the hydrogen (H) is linked to the carbinol, then dihydroxyacetone, $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{OH}$, results.

All the three compounds named are known to be sweet. The group $-\text{CO}.\text{CHOH}$ —(H) is then a glucophore. The hydrogen (H) simply indicates that the group must be united with one atom of hydrogen at least, in order to become a glucophore.

3. $\text{CO}_2\text{H}.\text{CHNH}_2$ — From the third glucophore most of the sweet amino acids may be derived in a similar way. We know aminoacetic acid, $\text{CH}_2\text{NH}_2.\text{CO}_2\text{H}$, and α -alanine, $\text{CH}_3.\text{CHNH}_2.\text{CO}_2\text{H}$, to be sweet. Even higher α -amino acids, such as *dl*-leucin are sweetish. The group $\text{CO}_2\text{H}.\text{CHNH}_2$ — is therefore a glucophore.

4. CH_2ONO_2 — This is the first example of a glucophore containing but one carbon atom. It has been pointed out by Cohn (*Loc. cit.*, p. 411) that many compounds are known which evidently owe their taste to this group. Ethyl nitrate,

$\text{CH}_3\text{CH}_2\text{ONO}_2$, and isobutyl nitrate, $(\text{CH}_3)_2\text{CH}.\text{CH}_2\text{ONO}_2$, are representatives of this class.

5. CH_2-H_x . This glucophore is present in sweet compounds containing halogen bound to one carbon atom. The abbreviation H1 is general for chlorine, bromine, and iodine. Fluorine derivatives may be included possibly. The small index x refers to the number of halogen atoms in the glucophore. It may vary from one to three, the number of hydrogen atoms in the glucophore meanwhile decreasing from two to zero. An application of these principles is shown in the following two examples:—

Methyl iodide has the glucophore CH_2I — which agrees exactly with the general formula given. In this case, the I limits the abbreviation H1 to a single atom of halogen. The index x equals one. In respect to the hydrogen, the index $3-x$ becomes equal to two. Obviously, this represents the number of atoms of this element in the glucophore.

Chloroform has a glucophore, $-\text{CCl}_3$, which agrees exactly, as before, with the general formula. In this particular case H1 stands for Cl, the index becoming 3 for the chlorine. The H term in the formula completely disappears, a condition following logically from the simple assumptions made.

6. $\text{CH}_2-\text{H}_x-\text{CH}_2-\text{H}_y$. This glucophore is also present in sweet compounds containing halogen. In strict agreement with the former paragraph, the H1 is general for chlorine, bromine, iodine, and with doubt, fluorine. In respect to the indices, x may vary from one to three, and y from one to two. In consequence, the number of hydrogen atoms change at the same rate, but inversely. The following two examples will serve to make these relations clear:—

Ethylene bromide has the glucophore $\text{CH}_2\text{Br}.\text{CH}_2\text{Br}$ —, which satisfies the formula, since H1 is equivalent to Br and x and y are each equal to unity.

Pentachloroethane has the glucophore $\text{CCl}_3-\text{CCl}_2$ —. Here H1 is represented by Cl, while x becomes equal to 3, y to two. Since the H term disappears, this glucophore contains no hydrogen.

7. While the 6 glucophores mentioned are undoubtedly the most important it is probable that this list may be expanded considerably. There are strong indications that the following groups, for instance, may be included in the list:—

(a) $\text{CO}_2\text{H}.\text{CHNHCH}_3$ —, (H). Example: sarcosine, $\text{CH}_3\text{NH}.\text{CH}_2.\text{CO}_2\text{H}$, which, according to Volhard (*Ann.*, 1862, cxxiii., 262) has a sweetish taste.

(b) $\text{CH}_2\text{OHCH}_2.\text{CHOH}$ —, (H). Example: 1,3-propanediol, $\text{CH}_2\text{OHCH}_2.\text{CH}_2\text{OH}$, described as sweet by F. Gerenmont (*Ibid.*, 1891, xlviii., 371).

(c) CHONO —, (H). Example: ethyl nitrite—"sweet spirits of nitre." In view of the limited data at hand, we prefer to postpone a decision on this point.

Auxogluc.

Definition.—We define an auxogluc as an atom or radical which combined with any of the glucophores yields a sweet compound. We have so far been able to identify nine of these.

1. **Hydrogen.**—Some combinations of this atom

with different glucophores have been discussed already in the preceding paragraphs.

2. CH_3 —Several instances are cited already showing that this radical forms sweet compounds with glucophores, but we wish to point out that the halogen derivatives, especially, yield numerous examples of such combinations. Thus ethyl bromide and iodide are sweet, although the taste of the former is said by Fehling (Cohn, *Loc. cit.*, p. 128) to be "burning" while the taste of the latter is not stated at all.

3. CH_3CH_2 —Examples supporting this auxogluc are found in the literature, except in the case of glucophores containing halogens. We have been able to satisfy ourselves that it applies to those as well by tasting propyl bromide and propyl iodide. Both are sweetish as we expected.

4. $\text{CH}_3.\text{CH}_2.\text{CH}_2$ —At present but few compounds containing this auxogluc are known to be sweet. We include it in our list with due reservation.

5. $(\text{CH}_3)_2\text{CH}$ —Examples of combinations of this auxogluc with five of the six glucophoric groups are mentioned in the literature. The resulting substances are sweet with one notable exception. 3-Methylbutane-1,2-diol is said by F. Flawitzki (*Ann.*, 1875, clxxix., 351) to be "burning bitter." An investigation of this compound is under way.

6. CH_2OH —This auxogluc yields with the different glucophores some of the most important sweetstuffs. Substances containing it will be cited from each class.

7. and 8. $\text{CH}_2.\text{CHOH}$ — and $\text{CH}_2\text{OH}.\text{CH}_2$ —We have several instances to cite, especially in conjunction with the glucophores $-\text{CHNH}_2.\text{CO}_2\text{H}$ and $\text{CH}_2\text{OH}.\text{CHOH}$ —, which indicate strongly that these two radicals are really auxoglucs. The α -amino- γ -oxybutyric acid of Fischer and Blumenthal (*Ber.*, 1907, xl., 110) as well as the α -amino- β -oxybutyric acid of W. Sternberg (*Arch. f. Anat. Physiol.*, 1915, p. 226) are sweet. 1,2,3-Butanetriol and 1,2,4-butanetriol are other examples. The list, however, is far from being complete in this instance and much work has yet to be done in order to prove that these two radicals may actually be included in the list.

9. Finally, the radicals $\text{C}_n\text{H}_{2n+1}\text{O}_n$ of normal polyhydric alcohols seem to act as auxoglucs without exception. The fact that sugars and polyhydric alcohols are sweet need hardly be mentioned. The d -glucosaminic acid of Fischer and Tiemann (*Ber.*, 1894, xxvii., 142) is a good example (C. Neuberg, *Ber.*, 1903, xxxv., 4013), proving that this holds true for the glucophore $\text{CO}_2\text{H}.\text{CHNH}_2$ — also.

Classification of the Auxoglucs.

As will be seen from the foregoing, the auxoglucs determined may be classified conveniently under four heads:—

1. Hydrogen.

2. The radicals $\text{C}_n\text{H}_{2n+1}$ of saturated hydrocarbons, in which $n=1-3$ (or 5).

3. The radicals $\text{C}_n\text{H}_{2n+1}\text{O}$ of monohydric alcohols in which $n=1-2$.

4. The radical $\text{C}_n\text{H}_{2n+1}\text{O}_n$ of normal polyhydric alcohols, in which $n=2-5$.

It is very probable that this list may be enlarged considerably. The ether radical CH_2CH —, for

LO

instance, may probably be included. But it is not permissible to do this until more experimental data can be obtained. Hasty generalisations easily lead to wrong conclusions, especially in this field. Faulty or conflicting observations on the subject are pretty numerous and due largely to individual differences in the sense of taste. Besides we do not yet know all the factors which tend to make compounds containing a glucophore taste bitter, and the source of notable exceptions.

The Influence of Acid Radicals.

We have just seen that all the saturated alkyl groups containing from one to three carbon atoms may act as auxoglucs. All of the higher paraffins do by no means act in the same way. Normal octyl iodide, for instance, is not sweet. Nor do all derivatives of the first members of the paraffin series act as auxoglucs. Glyceric acid, for instance, contains the glucophore $\text{CH}_2\text{OH}.\text{CHOH}-$, yet the presence of the acid radical $-\text{CO}_2\text{H}$ not belonging itself to a glucophore, causes the resulting compound to taste sour. The radicals of the lower fatty acids as well as the radicals of oxyacids yields, with a glucophore, acid compounds.

The Influence of the Phenyl Group.

As has been pointed out repeatedly by Cohn (*Loc. cit.*), the entrance of a phenyl radical tends to make an otherwise sweet compound bitter. Glycol is sweet, styrol is slightly bitter. There seem to exist quite a number of radicals which yield with a glucophore bitter compounds, but in view of the limited data on hand, we have to postpone the discussion of the rules governing this change of taste.

The Influence of Stereoisomerism.

Some seeming exceptions to our rule are due to stereoisomerism.

Thus, *L*-valin $(\text{CH}_3)_2\text{CH}.\text{CHNH}_2.\text{CO}_2\text{H}$, is made up of the glucophore $-\text{CHNH}_2.\text{CO}_2\text{H}$ and the auxogluc $(\text{CH}_3)_2\text{CH}-$ and might be expected to be sweet. According to E. Fischer (*Ber.*, 1906, xxxix., 2328), it is insipid and weakly bitter. However, the *D*-valin, and consequently the *DL*-valin too, are sweet.

It follows, therefore, that the racemic α -amino acids, but not all the optically active α -amino acids fall within the scope of our theory.

Determination of the Taste of an Organic Compound.

If then we wish to predict whether a given compound is sweet or not, we first will determine if it contains a glucophore. If not, we may conclude immediately that the substance is not sweet.

But even if we find the substance under consideration to contain a glucophoric group, we have to determine further whether an auxogluc is present too, or if the substance contains perchance an acid radical. In the former case the substance will be sweet, in the latter sour.

A few examples will make this clear.

Serin, $\text{CH}_2\text{OH}.\text{CHNH}_2.\text{CO}_2\text{H}$, may be divided in two parts, $\text{CO}_2\text{H}.\text{CHNH}_2-$ and $\text{CH}_2\text{OH}-$. The former we have seen to be a glucophore, the latter is an auxogluc. The compound made up of two such parts should be sweet, a conclusion which agrees with the facts.

Isoserin, $\text{CH}_2\text{NH}_2.\text{CHOH}.\text{CO}_2\text{H}$, although made up of the same atoms and "sapophores" (Cohn), does not contain the same glucophore from the standpoint of our theory, and consequently it should not be sweet. In the literature it is described as "insipid" (E. Fischer and W. E. Jacobs, *Ibid.*, 1907, xl., 1057, 1064).

α -Amino-butyric acid, $\text{CH}_3\text{CH}_2.\text{CHNH}_2.\text{CO}_2\text{H}$, is made up of the glucophore, $\text{CO}_2\text{H}.\text{CHNH}_2-$ and the auxogluc, CH_3CH_2- , and consequently it is sweet. On the contrary aspartic acid, $\text{CO}_2\text{H}.\text{CH}_2-\text{CHNH}_2.\text{CO}_2\text{H}$, while containing the same glucophore, is linked to an acid radical and it tastes sour.

Acetylene tetrabromide is made up of the glucophoric group $\text{CHBr}_2.\text{CBr}_2-$ and hydrogen as auxogluc. In accordance with our theory it should be sweet. A careful test convinced us that in alcoholic solution it tastes disagreeably sweetish.

1,2-Propanediol is sweetish. It contains the glucophore $\text{CH}_2\text{OH}.\text{CHOH}-$ and the auxogluc CH_3- .

The monomethyl ether of glycol, $\text{CH}_2\text{OH}.\text{CH}_2\text{OCH}_3$, on the contrary, does not contain a as tasteless (M. H. Palonua, *Ber.*, 1902, xxxv., 3300).

Finally, we select a member of the sugar group. Glucose is made up of the glucophore $\text{CH}_2\text{OH}.\text{CO}-$ and the auxogluc $\text{CH}_2\text{OH}(\text{CHOH})_5-$, the latter corresponding to the general formula $\text{C}_6\text{H}_{12}+\text{10}^{\circ}$.

The tables following, not only will include the necessary literary references to the above examples, but to a great number of other substances of this kind in addition. It is true that some of the derivatives included in our list are said to be bitter or tasteless. We question, however, some of these statements and we have already found them in several instances to be based on inaccurate observation.

Limitations and Possibilities of Our Theory.

It was pointed out at the beginning of this article that we confined the application of our theory at first to the more important sweet aliphatic compounds. The numerous cases in which the theory was verified seem to justify its publication, although we are well aware that there exist apparently some notable exceptions to our rule.

We hope to extend the scope of our theory soon. The combination of two glucophores, for example, seem to be sweet in most cases, i.e., a glucophore may act probably as an auxogluc also.

We further intend to apply our theory, with certain modifications, not only to sweet aromatic compounds, such as the saccharine of Remsen, but also to bitter substances in general. This study will require considerable time and work.

We finally have the pleasure to thank Professor Dr. R. E. Swain for interest and encouragement kindly given us in connection with this study.

Taste Trials.

Methyl iodide, CH_3I .—Prepared after Dumas and Peligot (*Ann.*, xv., 30), by treating methyl alcohol with red phosphorus and iodine. B.p. 43°. Taste: sweetish.

TABLE I.—Glucophore $\text{CH}_2\text{OH}-\text{CHOH}-$.

Auxogluc.	Name.	Taste.	Literature.
H—	Glycol	Sweet	A. Wurtz, <i>Ann. chim. phys.</i> , [3] 1857, lv., 410.
CH_3-	1,2-Propanediol	Sweetish	A. Wurtz, <i>Ibid.</i> , [3] 1857, lv., 439
CH_3CH_2-	1,2-Butanediol	Sweetish	N. Grabowski and A. Saytzeff, <i>Ann.</i> , 1875, clxxix., 333.
$(\text{CH}_3)_2\text{CH}-$	3-Methylbutane-1,2-diol	Burning bitter	E. Flawitzki, <i>Ibid.</i> , 1875, clxxix., 353.
$\text{CH}_2\text{OH}-$	Glycerol	Sweet	Scheele, <i>Crell's, Ibid.</i> , 1784, i., 99.
$\text{CH}_3\text{CHOH}-$	1,2,3-Butanetriol	Sweet	Beilstein, <i>Org. Chem.</i> , i., 277.
$\text{CH}_2\text{OHCH}_2-$	1,2,4-Butanetriol	Sweet	G. Wagner, <i>Ber.</i> , 1894, xxvii., 2437.
$\text{CH}_3\text{CH}_2\text{CHOH}-$	1,2,3-Pentanetriol	Sweet	G. Wagner, <i>Ibid.</i> , 1888, xxi., 3349.
$\text{C}_n\text{H}_{2n-2}$	Polyhydric alcohols	All sweet	Cohn, <i>Loc. cit.</i> , pp. 212, 219, 224.

TABLE II.—Glucophore, $-\text{COC}-\text{HOH}-(\text{H})$.

Auxogluc.	Name.	Taste.	Literature.
H—	Glycollic aldehyde	Distinctly sweet	Abderhalden, <i>Bioch. Handb.</i> , ii., 266.
CH_3-	Oxyacetone	Sweet	A. Kling, <i>Ann. chim. phys.</i> , 1905, [8] v., 496.
	Oxypropionic aldehyde monomolecular	Unknown	
	bimolecular	Slightly bitter	A. Wohl, <i>Ber.</i> , 1908, xli., 3609.
$\text{CH}_2\text{OH}-$	Glyceric aldehyde monomolecular	Sweet and bitter	A. Wohl, <i>Ibid.</i> , 1898, xxxi., 1801.
	bimolecular	Slightly sweet	A. Wohl, <i>Ibid.</i> , 1898, xxxi., 2394.
	Dioxyacetone	Sweet	O. Piloty, <i>Ibid.</i> , 1897, xxx., 3165.
$\text{CH}_3\text{CHOH}-$	Methyl-glyceric aldehyde $\text{CH}_3(\text{CHOH})_2\text{CHO}$	Sweet and bitter	A. Wohl and F. Franz, <i>Ibid.</i> , 1902, xxxv., 1908.
	Methyl-dioxyacetone	Sweetish	O. Diehls and E. Stephan, <i>Ibid.</i> , 1909, xlii., 1788.
$\text{C}_n\text{H}_{2n-2}\text{O}_n$	Sugars, e.g., hexoses	Sweet	Common knowledge.

TABLE III.—Glucophore, $\text{CO}_2\text{H}-\text{CHNH}_2$.

Auxogluc.	Name.	Taste.	Literature.
H—	Amino-acetic acid	Sweet	E. Abderhalden, <i>Bioch. Handb.</i> , iv., 403.
CH_3-	<i>dl</i> - α -Amino-propionic acid	Sweet	A. Strecker, <i>Ann.</i> , 1850, lxxv., 31.
CH_3CH_2-	<i>dl</i> - α -Amino-butyric acid	Sweet	C. Frideel and V. Nachuch, <i>Ann. Suppl.</i> , 1861, ii., 71.
$\text{CH}_3(\text{CH}_2)_2-$	<i>dl</i> - α -Amino- <i>n</i> -valeric acid	Sweet	A. Lipp, <i>Ann.</i> , 1882, ccxi., 360.
$(\text{CH}_3)_2\text{CH}-$	α -Amino-isovaleric acid (<i>dl</i> -valin)	Sweet	M. D. Slimmer, <i>Ber.</i> , 1902, xxxv., 400.
$(\text{CH}_3)_2\text{CHCH}_2-$	<i>dl</i> -leucine	Slightly sweet	Tierfelder, <i>Handbuch</i> , p. 235.
$\text{CH}_2\text{OH}-$	<i>dl</i> -Serine, α -amino- β -hydroxy-propionic acid	Sweet	Schmidt, <i>Pharm. Chem.</i> , i., 460.
$\text{CH}_3\text{CHOH}-$	<i>dl</i> - α -Amino- β -hydroxy-butyric acid	Sweet	W. Sternberg, <i>Arch. Anat. Physiol.</i> , 1905, 228.
$\text{CH}_2\text{OH.CH}_2-$	<i>dl</i> - α -Amino- γ -hydroxy-butyric acid	Sweet	E. Fischer and Blumenthal, <i>Ber.</i> , 1907, xl., 110.
$\text{CH}_3\text{CHOH.CH}_2-$	<i>dl</i> - α -Amino- γ -hydroxy-valeric acid	Very sweet	E. Fischer and Leuchs, <i>Ibid.</i> , 1902, xxxv., 3797.
$\text{C}_n\text{H}_{2n-1}\text{O}_n$	<i>d</i> -Glucosaminic acid	Agreeably sweet	E. Fischer and F. Tiemann, <i>Ber.</i> , 1894, xxvii., 142. C. Neuberg, <i>Ibid.</i> , 1903, xxxv., 4013.

TABLE IV.—Glucophore CH_2ONO_2 .

Auxogluc.	Name.	Taste.	Literature.
CH_3-	Ethyl nitrate	Sweet	Millon, <i>Ann.</i> , 1843, xlvii., 374. G. Berton, <i>Gazz. chim. ital.</i> , 1890, xx., 373.
$\text{CH}_3(\text{CH}_2)_2-$	Butyl nitrate	Sweet	G. Berton, <i>Ibid.</i> , 1890, xx., 373. Cohn, <i>Loc. cit.</i> , 1890, xx., 412.
$(\text{CH}_3)_2\text{CH}-$	Isobutyl nitrate	Sweet	A. Wurtz, <i>Ann.</i> , 1855, xciii., 120.
$(\text{CH}_3)_3\text{CHCH}_2-$	Isoamyl nitrate	Sweetish	W. Hofmann, <i>Ibid.</i> , 1848, lxxviii., 333.
$\text{CH}_2\text{OH}-$	Glycol mononitrate	Sweet	Fehling, <i>Handwörterbuch der chemie</i> , vi., 1273. L. Henry, <i>Ann. chim. phys.</i> , 1872, [4] xxvii., 242.

TABLE V.—Glucophore $\text{CH}_2^{\text{H}_2\text{---x}}$

Auxogluc.	Name.	Taste.	Literature.
H—	Methyl chloride	Sweetish	Fehling, <i>Loc. cit.</i> , iv., 401. Cohn, <i>Loc. cit.</i> , p. 123.
	Methylene chloride	Sweetish	W. H. Perkinsen, <i>J. Chem. Soc.</i> , 1869, [2] vii., 260. A. Butlerow, <i>Jahresb.</i> , 1869, 343.
	Chloroform	Sweet	W. Sternberg, <i>Z. Anat. Physiol.</i> , 1905, p. 119.
	Methylene bromide	Sweet	L. Henry, <i>Ann. chim. phys.</i> , 1883, [5] xxx.
	Bromoform	Sweetish	Kolbe, i., 601. Cohn, <i>Loc. cit.</i> , p. 130.
	Methyl iodide	Sweet	Oertly and Myers.
	Methylene iodide	Sweet	A. Butlerow, <i>Compt. rend.</i> , 1858, xli., 595.
	Iodoform	Sweetish	Schmidt, <i>Pharm. Chem.</i> , i., 108.
	Chlorobromo-methane	Sweetish	L. Henry, <i>Compt. rend.</i> , 1885, ci., 599.
	Chlorodibromo-methane	Sweetish	Cohn, <i>Loc. cit.</i> , p. 130.
	Dichloro-iodo-methane	Sweetish	A. Borodine, <i>Ann.</i> , 1863, cxxvi., 239.
	Bromo-iodo-methane	Sweetish	L. Henry, <i>Compt. rend.</i> , 1885, ci., 599.
CH ₂ —	Ethyl chloride	Sweetish	Fehling, p. 126. Cohn, <i>Loc. cit.</i> , p. 126.
	Ethylidene chloride	Sweetish	A. Geuther, <i>Ann.</i> , 1888, cv., 324.
	Ethyl bromide	Burning	Fehling, <i>Loc. cit.</i> , p. 124. Cohn, <i>Ibid.</i> , p. 128.
		Sweet	Oertly and Myers.
	Ethyl iodide	Sweet	Oertly and Myers.
	1,1-Chloro-bromo-ethane	Sweetish	W. Staedel and J. Denzel, <i>Ann.</i> , 1879, cxv., 193.
CH ₂ —	1,1-Chloro-iodo-ethane	Sweet	M. Simpson, <i>Pharm. Zentralk.</i> , xxvii., 424.
	1,1-Bromo-iodo-methane	Sweet	M. Simpson, <i>Pharm. Zentralk.</i> , xxvii., 424.
CH ₂ CH ₂ —	1-Chloropropane	Sweetish	Oertly and Myers.
	1-Bromopropane	Sweet	Oertly and Myers.
	1-Iodopropane	Sweetish	Oertly and Myers.
		taste develops tardily	
CH ₂ CH—	Isobutyl chloride	Sweetish	Pierre and E. Puchot, <i>Ann.</i> , 1872, clxiii., 276.
CH ₂ OH—	Ethylene chlorohydrine	Sweet	A. Butlerow, <i>Ibid.</i> , 1867, cxliv., 42.
	Ethylene bromohydrine	Bitter	L. Henry, <i>Ann. chim. phys.</i> , 1872 [4] xxvii., 252.
	Ethylene iodohydrine	Sweet	A. Butlerow and M. Ossekin, <i>Ann.</i> 1867, cxliv., 44.
		Bitter	L. Henry, <i>Bull. Belg.</i> , [3] 183.
	2,2-Dibromo-ethane-1-ol	Sweet as sugar	E. Demole, <i>Ber.</i> , 1876, ix., 50.
CH ₂ .CHOH—	1-Chloropropane-2-ol	Sweetish	Oser, <i>Jahresb.</i> , 1860, p. 448.

TABLE VI.—Glucophore $\text{CH}_2^{\text{H}_2\text{---x}} - \text{CH}_2^{\text{H}_2\text{---x}}$

Auxogluc.	Name.	Taste.	Literature.
H—	Ethylene chloride	Sweetish	Fehling, <i>Loc. cit.</i> , i., 154.
	Ethylene bromide	Sweetish	Fehling, <i>Ibid.</i> , i., 1153.
	Ethylene chloro-iodide	Sweet	M. Simpson, <i>Ann.</i> , 1863, cxxv., 102.
	1,1-Dichloro-2-iodo-ethane	Sweet	L. Henry, <i>Compt. rend.</i> , 1884, xcvi., 518.
	1,1,2,2-Tetrachloro-ethane	Sweet	E. Paterno and G. Pisati, <i>Jahresb.</i> , 1871, 508.
	1,1,1-Trichloro-2-bromo-ethane	Sweetish	L. Henry, <i>Compt. rend.</i> , 1884, xcvi., 370.
	1,1,2,2-Tetra-bromo-ethane	Nearly tasteless	Cohn, <i>Loc. cit.</i> , p. 132.
		Sweetish	Oertly and Myers.
CH ₂ —	Pentachloro-ethane	Sweet	J. Pierre, <i>Jahresb.</i> , 1847, pp. 48, 686.
	2-Chloro-1-iodopropane	Sweet	M. Simpson, <i>Ann.</i> , 1863, cxxvii., 337.
	2-Chloro-1,2-dibromo-propane	Sweet	C. Friedel, <i>Ann.</i> , 1859, cxii., 236.
CH ₂ OH—	2,3-Dichloro-1-hydroxypropane	Burning spicy	B. Tollens, <i>Ibid.</i> , 1870, clvi., 165.
	2-Chloro-3-bromo-propane-1-ol	Sweet	L. Henry, <i>Bull. Belg.</i> , [2] 37, 370.

Ethyl bromide, $\text{CH}_3\text{CH}_2\text{Br}$.—Prepared according to de Vries (*Jahrb. Chem.*, 1857, 441) by distilling ethyl alcohol with sulphuric acid and sodium bromide. B.p. 38–39°. Taste: sweet.

Ethyl bromide, $\text{CH}_3\text{CH}_2\text{I}$.—Prepared according to Serullas (*Ann. chim. phys.*, 1829, [2] xlii., 119) by treating ethyl alcohol with phosphorus and iodine. B.p. 72–73°. Taste: sweet.

1-Chloropropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$.—Prepared according to I. Pierre and E. Puchot (*Ann.*, 1872,

clxiii., 266), by treating primary propyl alcohol with phosphorus trichloride. B.p. 46–47°. Taste: sweetish.

1-Bromopropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$.—Prepared according to E. Linnemann (*Ibid.*, 1872, clxi., 40) by distilling primary propyl alcohol with sulphuric acid and sodium bromide. B.p. 71°. Taste: sweet.

1-Iodopropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$.—Prepared according to M. Chancel (*Bull. soc. chim.*, 1883,

xxxix., 648) from primary propyl alcohol, red phosphorus, and iodine. B.p. 102° . Taste: sweetish. Taste develops tardily.

1,1-, 2,2-, Tetrabromoethane, $\text{CHBr}_2\text{CHBr}_2$.—Prepared according to W. Muthmann (*Kryst. Min.*, 1899, xxx., 73), by treating acetylene (made from calcium carbide) with bromine. The raw product was successively washed with water, sodium carbonate, sodium thiosulphate, and with water again. It was then extracted with ether, dried with calcium chloride, and the ether distilled off. Finally, the acetylene tetrabromide was rectified by distilling *in vacuo*. B.p. 134° at 33 mm. Taste: sweetish and disagreeable when first placed on tip of tongue; to many people it tastes only disagreeably. Taste of a solution in alcohol, 60 per cent; disagreeably sweetish.

Classification of Aliphatic Sweetstuffs According to Glucophores and Auxoglucs.

In our new classification of aliphatic sweetstuffs, the substances are first sub-divided in different classes, according to their glucophores. Thus all substances that owe their sweet taste to the glucophore $\text{CH}_2\text{OH}\cdot\text{CHOH}\cdot$ are to be found in Table I. Within each table the sweetstuffs are arranged according to their auxoglucs.

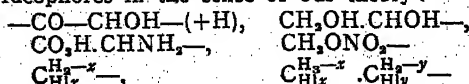
In order to locate a given sweet compound, determine first its glucophore and its auxogluc by the method previously described. Then examine lists for the corresponding glucophore and auxogluc, the latter to be found in the first column of each table.

If the substance be sweet and there is no space for it in the table, its taste is not yet known, as far as we can ascertain; or it does not fall within the present scope of our theory.

Summary.

1. A theory has been worked out relating the sweet taste of organic compounds to their constitution. The taste was found to be dependent on two factors. The glucophores make a given compound a potential tastestuff. If a glucophore is bound to any of the auxoglucs, a sweet compound results.

2. The following radicals are found to be glucophores in the sense of our theory:—



Some others may very likely be included later on.

3. The following atoms or radicals seem to act as auxoglucs, yielding with glucophores sweet compounds:

(a) H, hydrogen.

(b) The radicals $\text{C}_n\text{H}_{2n+1}\text{O}\cdot$ of saturated hydrocarbons, containing from one to three carbon atoms. Example $\text{CH}_3\text{CH}_2\cdot$.

(c) The radicals $\text{C}_n\text{H}_{2n+1}\text{O}\cdot$ of monohydric alcohols, n being equal to one or two. Example $\text{CH}_2\text{OH}\cdot$.

(d) The radicals $\text{C}_n\text{H}_{2n}\text{O}_2\cdot$ of polyhydric alcohols. Example $\text{CH}_2\text{OHCHOH}\cdot$.

4. Numerous examples supporting this theory are cited, and a new classification of sweet aliphatic compounds is proposed.

5. An outline of plans for future work on our theory is given.

MINERAL RESOURCES OF THE WORLD.

THE Imperial Mineral Resources Bureau in a pamphlet entitled "The Mineral Industry of the British Empire and Foreign Countries," gives statistical and technical information concerning the mining or quarrying of minerals during the period 1913-1919.

Fuller's Earth.

In a short paragraph giving the general properties, nature, &c., of Fuller's Earth, the mineral is described as a clay-like material, usually non-plastic and of a greyish, yellowish, greenish or bluish colour. Its chemical composition is essentially a complex aluminium silicate, with variable amounts of iron oxide, magnesia, lime and alkalis.

Its uses include:—as a filler for paper; as a carrier for certain pigments; as an ingredient for some soaps; its chief uses being for the removal of grease from woollen goods and for the decolorisation and clarification of oils.

The chief sources of supplies are England and the United States of America. Table I. gives the production in the United Kingdom.

Numerous analyses of Fuller's Earth mined at different places are given, of which some are reproduced in Table II.

In an appendix is given a statement on the supposed nature of Fuller's Earth. According to Dr. A. H. Cox, who has studied this subject from the petrological side, Fuller's Earth represents a true precipitate, thus accounting for its occurrence as an extremely uniform and fine-grained deposit interbedded with coarse sands.

TABLE I.—Production of Fuller's Earth.

County.	1913	1914	1915	1916	1917	1918	1919
Bedford (from mines) ...	640	630	590	—	—	—	—
Gloucester (from mines) ...	—	—	—	—	—	—	495
Somerset (from mines) ...	3,559	4,256	4,425	5,577	4,109	3,783	3,469
Surrey (from quarries) ...	27,410	32,976	24,283	23,529	23,807	19,507	20,821
TOTAL	31,609	37,862	29,298	29,106	27,916	23,290	24,785

TABLE II.—Analyses of Fuller's Earth.

	Nutfield. Earth.	UNITED KINGDOM. Midford. Blue Earth.	Woburn. Yellow Earth.	AUSTRALIA. Wingew. N.S.W.	UNITED STATES. Bodenner's Pit, Fairbarn.	D. Henault Custer City.
Silica	58.66	54.0	56.9	50.61	68.23	55.45
Alumina	17.33	18.6	15.7	19.35	14.93	18.58
Ferric oxide	7.21	3.9	9.5	3.55	3.15	3.82
Ferrous oxide	—	0.8	0.1	n.s.	n.s.	n.s.
Lime	3.17	7.0	2.1	1.37	2.93	3.40
Magnesia	3.26	2.3	2.7	3.24	0.875	3.50
Soda	1.03	0.7	0.3	0.47	n.s.	n.s.
Potash		1.8	0.7	0.92	n.s.	n.s.
Phosphoric anhyd.	n.s.	n.s.	n.s.	trace	n.s.	n.s.
Carbonic acid	—	3.4	—	n.s.	n.s.	n.s.
Moisture	n.s.	n.s.	n.s.	13.73	6.20	8.80
Combined water	n.s.	n.s.	n.s.	6.45		
Loss on ignition (not includ- ing carbonic acid)	8.74	7.2	11.9	n.s.	n.s.	n.s.
		99.7	99.9	99.69	96.315	93.55

NOTE.—Those marked n.s., no analysis is given.

PROCEEDINGS OF SOCIETIES.

INSTITUTE OF METALS.

Annual Meeting, September 15, 1920.

(Concluded from 155.)

"Service Experience with Condensers." By Engineer Lieutenant-Commander G. D. ALLEN, R.N., Member (London).

With the introduction of the water-tube boiler into the Navy condenser defects assumed an increasing degree of prominence, and although the proportionate number of failures is very small, the results attending such an apparently trivial matter as a small perforation may be out of all proportion to the magnitude of the defect itself.

The paper traces the growth of the prominence of such defects, and gives examples of past causes of failure which have been eliminated by mechanical precautions. Present causes of failure are discussed, with a view to showing that although the main problem is to provide immunity from corrosive action, marine condenser tubes are subject to other causes of failure and must be possessed of properties other than that of resistance to corrosion.

The paper concludes with remarks on such experience as has been gained with various protective treatments and processes and with alloys other than the Admiralty mixture.

"Some Features in the Behaviour of Beta Brass when Cold-Rolled." By F. JOHNSON, M.Sc., Member (Birmingham).

A description is given of the mechanical properties of a brass containing 55.6 per cent copper (made from electrolytic copper and electrolytic zinc) before and after cold-rolling. The alloy consisted entirely of crystals of the beta phase, no free alpha being observable, although if cooled under equilibrium conditions some alpha should accompany the beta.

A reduction of 50 per cent in rolling (cold) resulted in the raising of the tensile strength from 22.6 to 38.2 tons per square inch, the percentage elongation falling from 27 to 8½ per cent.

An interesting feature of the micro-structure of the cold-rolled alloy was the occurrence of a maze

of dark lines, which persisted after re-polishing and re-etching. These lines represent planes of displacement and they "fault" one another, as clearly shown in the photo-micrographs.

They are of a higher degree of magnitude than slip bands or "etch-bands" which are the etching-record of slip-bands. The author suggests that they belong to the same category as the Neumann bands named after the investigator who discovered them in meteorites, and the existence of which has been proved in terrestrial iron (ferrite) subjected to shock. On a cleavage face these bands are parallel either to the diagonals of a square or to the linen which join the angles of a square to the centre of the opposed edges. These correspond to the faces of the trapezohedron.

The author gives some indications of the crystallographic features of the cube, octahedron, rhombohedron, and trapezohedron, and the measurement of some of the angles formed on a random face by the deformation bands produced in the sample of cold-rolled beta brass.

Low temperature annealing results in the crystallisation of the alpha phase along the crystallographic planes of displacement, but high-temperature annealing (in the stability-region of the beta phase) results in the disappearance both of the deformation bands and of the post-deformation alpha. No refinement of grain results from the low-temperature annealing which, however, causes an almost complete restoration of the mechanical properties originally associated with the unrolled alloy. The deposition of alpha along the planes of displacement caused by low-temperature annealing recalls the explanation offered by Osmond and Cartland of the amelioration of mild steels by quenching and tempering.

Reference is also made to a curious stratification, visible to the naked eye, which cold-rolling develops in the alloy and which is revealed on a sawn face.

"Note on a Failure of Manganese Bronze." By J. H. S. DICKENSON, Member (Sheffield).

Examination of a "Manganese Bronze" End Plate from a turbo alternator rotor which failed in service showed that certain fractured peripheral projections had been rendered brittle by the contact of fluid solder which had penetrated along the junctions of the crystalline grains.

The end plate was shown by analysts and micro-examination to be a typical beta brass of simple polyhedral structure. Bend tests taken from the inner, unaffected portions, showed toughness and ductility whether tested at the room temperature or as high as 200° C., but collapsed instantly under small loads, with an intergranular fracture and no appreciable distortion, if heated sufficiently to melt the point of a stick of soft solder applied to the side in tension. No such effect was obtained when solder was melted on the side in compression, or when a test piece was soldered on the tension side and stressed with the solder in the solid state. It was found that there had been local heating in the rotor and the solder appeared to have penetrated while the beta brass end plate was running under stress.

An investigation followed to elucidate the conditions under which alloys of the "Manganese Bronze" type, *i.e.*, beta brasses, as well as alpha and mixed brasses, are prejudicially affected by contact with fluid solders, the special points on which information was required being to ascertain the stress required to produce failure, and also to what extent variation in composition and micro-structure affected the result.

The effect of bringing fusible alloys (melting at 69.5° C. and 93° C.), soft tin-lead solder, and tin into fluid contact with heated and stressed test bars of various kinds of brass has been ascertained. In all cases the result was greatly to reduce the maximum stress and cause intergranular fracture, this being by far the most marked in the case of beta brasses of simple polyhedral structure, less so when alpha and beta constituents occur together, and to nothing like the same extent in alpha brass with interlocking crystalline grains. These differences form a further example to show the danger of permitting metallic crystals to develop smooth and irregular outlines. It is suggested that further work in this direction may throw additional light on the phenomenon of season cracking.

"The Allotropy of Zinc." By KATHLEEN E. BINGHAM, B.Sc., Member (Teddington).

This paper reviews briefly some of the previous work on the allotropy of zinc and gives an account of the author's own research. While some of the observations in this research gave negative results (*e.g.*, thermal I.M.F. measurements and thermal curves), yet on considering the larger part of the evidence, it is difficult to avoid the conclusion that zinc exists in three allotropic forms.

The breaks in the resistance temperature curves are so slight as to suggest that the electrical resistance of zinc is hardly affected by the allotropic changes. Observations on quenched material of some of the properties indicate approximately the temperatures of the critical changes as follows:—

	Degrees C.	Degrees C.
Electrolytic Potential	180 (?)	330 to 340
Specific Gravity	170	—
Hardness	160	330
Mechanical Properties:		
Maximum Stress	180	310
Elongation	180	310

Tensile tests at high temperatures give strong confirmation of the critical changes at 190° C.

and 300° C. (maximum stress) and 160° C. to 180° C. (elongation).

The micro-structure shows one system of crystal boundaries in the χ range of temperature, two interpenetrating systems in the β range, and three in the ν range. It has been shown also that re-crystallisation takes place on heating the cast material and cooling it slowly from below the melting point to the ordinary temperature; a further indication that some allotropic change occurs.

NOTES.

APPOINTMENT.—Prof. John Bretland Farmer, D.Sc., M.A., F.R.S., Imperial College of Science and Technology, has been appointed by an Order of Council dated the 28th day of August, 1920, to be a member of the Advisory Council to the Committee of the Privy Council for Scientific and Industrial Research.

RAT EXTERMINATOR FOR THE UNITED STATES.—His Majesty's Consul at Portland, Oregon (Mr. John P. Trant), reports that in view of the present rat epidemic and the need for an efficient exterminator at Oregon and elsewhere in the United States, where a great menace of plague from rat infested districts exists, there is an excellent opportunity for the introduction of an effective virus of British manufacture, which would probably be welcomed if delivery is prompt and results are satisfactory. If interested in this market for rat exterminator, communicate with His Majesty's Consul at Oregon, preferably forwarding samples for experimental purposes.

PORTSMOUTH MUNICIPAL COLLEGE.—Principal: Oliver Freeman, Wh.Sc., A.R.C.S., B.Sc. Head of Chemistry and Natural Science Department: W. H. Watson, M.Sc., A.R.C.S.—The Department provides full courses of instruction in Chemistry and Botany for B.Sc. degree (Pass and Honours) and for other professional examinations. Special provision is also made for Metallurgy and Pharmacy. The Department is recognised by the Pharmaceutical Society of Great Britain and there are complete courses for the Qualifying Examination of the Society (Parts I. and II.), but there are no vacancies in the day classes in this section until next year. Evening classes are also held in the principal subjects taught in the Department. Prospectus of Day or Evening Classes can be had from the Secretary.

PROPRIETARY MEDICINES BILL.—(1) The object of this Bill is to give effect to the recommendations of the Select Committee of the House of Commons on Patent Medicines, who reported in August, 1914: *see* Paper 414 of 1914. It contains no provisions which were not specifically recommended by the Select Committee, and it includes all their more important recommendations so far as they fall within the province of the Ministry of Health. (2) Provision is made for the establishment of a register of proprietary medicines and appliances, and of the owners thereof, and the Bill prohibits the sale of any unregistered proprietary medicine or appliance. The expression "proprietary medicine" is defined in the Bill to mean a medicine

which is held out by advertisement as of use for curative or remedial purposes, and which is either sold under a trade name or manufactured by a secret process. Severe penalties are attached to the unauthorised disclosure by the registrar or any other person of the formula of any registered medicine. (3) The sale of remedies purporting to cure certain diseases, such as consumption or cancer, is prohibited, and it is made an offence to advertise any article in terms which suggest that it can be used to produce abortion. (4) The Minister of Health is empowered to remove from the register any injurious medicine or appliance, but the owner is given a right of appeal to the High Court. (5) The Bill, in accordance with the recommendations of the Select Committee, prohibits certain practices, chiefly in connection with advertisements, which the Committee considered undesirable. (6) All regulations made under the Bill are required to be laid before Parliament.

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3156.

FIFTH ANNUAL REPORT OF THE COMMITTEE OF THE PRIVY COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH.

I. As five years have now passed since the inception of the scheme for the organised Encouragement by the State of Scientific and Industrial Research, the introduction to this Report contains a review of the work which has been done during this period.

The programme of the Department can now be laid out with considerable precision. It falls under four main heads: (a) the encouragement of the individual research worker, particularly in pure science; (b) the organisation of national industries into co-operative research associations; (c) the direction and co-ordination of research for national purposes; and (d) the aiding of suitable researches undertaken by scientific and professional societies.

II.—*The Encouragement of Individual Research Workers.*

It is again emphasised, as in previous reports, that "industrial research organisations are essentially man-consuming as distinguished from man-producing agencies," and that the only organised training grounds for the research worker are the universities. Attention is directed to the fact that these institutions are overcrowded with students, while their research laboratories are being used for the instruction of undergraduates, and the demand for teachers exceeds the supply.

Although it is not the function of the Department to make grants to universities, it makes grants to suitable research workers and students whether they are in universities or elsewhere.

Since the establishment of the Department, 136 maintenance grants have been made to students, and 89 to independent workers, 49 grants have been made to provide professors with competent research assistants, and 87 to give them laboratory or clerical assistance; during the same period 49 equipment grants have been made.

The development of assistance of this kind during the five years under review is indicated by the increase in the expenditure upon it. During the academic year 1916-17 this amounted to £3207; during the present year it is estimated at £26,700, and it is expected that during the coming year it will reach £45,000.

It is important to note that the great majority of the grants have been made for work in the fundamental sciences and that in these cases no conditions are attached either as to the line of work to be pursued or as to the use to be made of the results. In making grants to individuals, the Advisory Council are guided not so much by the theme as by the evidence before them of the scientific capacity of the worker. The Advisory

Council quote with agreement the view of Mr. Balfour that while the State can aid research it would only destroy research if it attempted to control it; at the same time they share the hope of Mr. Balfour that it does not follow that it is quite impossible to combine with the independence of the worker some better reward for the work he is doing.

III.—*The Organisation of Industries into Research Associations.*

Experience has shown that the plan of organising associations of industrial firms for the co-operative scientific investigation of their problems is sound, the present position being that 18 research associations have been established, while five others have been approved by the Department and will shortly receive licences from the Board of Trade. The 10 research associations actually at work have raised from their 2300 members an aggregate income of nearly £40,000 in their first year of existence, and it is anticipated that in succeeding years as their work develops they will raise still larger sums.

Out of the Million Fund granted by Parliament for research associations, £63,800 has already been expended, and it is estimated that the Department is committed to a total expenditure of nearly £450,000 on account of the established research associations, and to a further expenditure of at least £120,000 on account of those approved but not yet licensed.

Negotiations are now proceeding for the establishment of other research associations and the total commitments out of the Million Fund are expected shortly to reach £800,000.

In discussing the attitude of industries to research the Advisory Council refer to the possibility that results of greater value to industry might have been obtained if the Million Fund had been spent upon research at the National Physical Laboratory and other research laboratories rather than in making subventions to associations that have to buy staffs, equipment, and experience at a time when all three are scarce and dear. They point out, however, that it is only after industries have done research for themselves that they can appreciate either its difficulties or its value, and further that if the money had been spent on research directed by the Government itself, its effect upon manufacturers would have been destructive of their self-reliance. As it is, over 2500 firms have already guaranteed a minimum aggregate income for research of £38,400 a year for five years, and have shown already that they will considerably exceed their minimum guaranteed expenditure.

IV.—*The Conduct and Co-ordination of National Research.*

A considerable part of the introductory review of the early history of the Department is devoted to a description of the organisation of national research on problems which are of such wide application that no single industry can grapple with them effectively.

The first special organisation established for dealing nationally with a problem of this kind was the Fuel Research Board, which was appointed under the direction of Sir George Beilby, F.R.S., in 1917. This Board has drawn up a programme of research which provides for

the examination of the more important types of coal from all parts of the United Kingdom, and their classification according to their suitability for the production by different methods of solid, liquid, and gaseous forms of fuel. This classification includes the study of the carbonisation of coals at different temperatures and the determination of the quantities and qualities of the products, the work being carried out at the Fuel Research Station erected by the Department at East Greenwich. The work of the Board has been extended to cover the investigation of peat as a source of fuel, of the suitability of different kinds of coal for use as pulverised fuel, and of the problems of the production and utilisation of alcohol for power and traction purposes.

The enquiry of the Board into "Gas Standards" opened up the whole question of the future development of the gas industry, and on the adoption by Parliament of the method of basing the charges for gas on the number of thermal units it contains, as recommended by the Board, the equipment of the Fuel Research Station was extended in order to acquire trustworthy information as to the economics of gas production by new methods.

The Fuel Research Board are in close touch with the Petroleum Department, which is entrusted with all questions of fuel oil for national purposes; they are co-operating with the Manchester Corporation in a research on the efficiency of domestic grates, with the Ministry of Health in experiments on the efficiency of cooking ranges, and with the Atmospheric Pollution Committee of the Meteorological Office and the Smoke Prevention Committee of the Ministry of Health in investigations into the general problems of air pollution by smoke and dust.

The Geological Survey and Museum have been transferred from the Board of Education to the Department in order that the results of their work may form part of that knowledge which it is the function of the Department to create, co-ordinate, and place at the disposal of all other Departments. A Geological Survey Board has been appointed, and plans are being formulated for extending the work of the Survey to meet the increasing demands upon its services.

The Food Investigation Board, established under the direction of Mr. W. B. Hardy, F.R.S., has conducted most important researches into the biochemical and biophysical problems underlying the problems of cold storage and other means of preserving and handling fish, meat, fruit and vegetables. The Advisory Council have recommended that a grant should be given to the University of Cambridge for the erection and equipment of a low temperature research station to be maintained by the Department. This offer has been accepted by the University, which has placed a suitable and convenient site at the disposal of the Department.

In order to deal with research on the materials and construction of buildings, a Building (Materials and Construction) Research Board has been established under the Chairmanship of the Marquess of Salisbury. This Board is working in close co-operation with the Ministry of Health and other Government Departments concerned.

In view of the fact that the annual pre-war expenditure on building materials was about 35

million pounds in England and Wales, it is hoped that the work of this Board will result in great national savings, since comparatively small economies in the cost of building materials would at present prices represent a very large total sum.

The transfer to the Department of the National Physical Laboratory has enabled the Department to bring the great resources of this institution into their proper relation to the general scheme for the organisation of research. Month by month the National Physical Laboratory becomes of increasing value to the nation; and Government Departments, Research Associations, and Boards and Committees of the Department are constantly seeking its assistance. In 1914 its annual income was about £40,000; for the current year £203,000 has been provided, the Advisory Council being convinced that the money will be productive in the fullest sense.

A very important step has been taken during the current year by the decision of the Government to establish a series of co-ordinating Boards for the organisation of the scientific work needed for the fighting services so as to avoid unnecessary overlapping, to secure economy, to facilitate the exchange of knowledge between Departments, and to provide a single direction and financial control for all work of a fundamental nature of civilian as well as of military interest. Upon each of these Boards the fighting Departments and such civil Departments as are materially concerned are to be represented by responsible technical officers with whom individual scientific men are to be associated. The Boards are to be attached to the Department of Scientific and Industrial Research, upon whose vote the cost of the researches they direct is to be borne; this Department will also be responsible for arranging for the co-operation in the researches of industrial research associations wherever this is appropriate.

In the first instance, three Boards have been established, one for chemistry, one for physics, and the third for engineering; these, with the existing Radio Research Board, form the nucleus of the scheme.

Reference is made in this portion of the Report to the new Physics Laboratory erected by the Admiralty for their own work in the grounds of the National Physical Laboratory at Teddington.

On the appointment by the Air Ministry of the Aeronautical Research Committee, the respective responsibilities for research laid upon the Air Ministry and the Department of Scientific and Industrial Research were defined. While the Department of Scientific and Industrial Research is to be responsible for provision for independent research for the advancement of science, even though it ultimately tends to the advancement of aeronautics, the Air Ministry is to be responsible for research aiming exclusively at the advancement of aeronautics, excepting as regards work done at the National Physical Laboratory or by an Aircraft Industry Research Association, if and when established with the approval of the Department.

Pending the establishment of permanent machinery for the general co-ordination of Government Research, certain temporary arrangements for liaison between the Air Ministry and the Department of Scientific and Industrial Research have been made.

V.—*Aid to Scientific and Professional Societies.*

At the outset of their work, the Advisory Council were able to prevent a number of important researches undertaken by scientific and professional societies from being abandoned through lack of funds. The total grants made to organisations of this kind in respect of 69 researches during the five years under review amounted to £68,816. The financial assistance afforded to societies tends, however, to diminish, since some of the researches are being transferred to research associations and some to the Department itself; in the latter case the society often continues to assist by appointing a Supervising Committee; an additional reason for the diminution of the grants to societies is the fact that the call on their funds for aid for researches intended solely to increase knowledge has been lessened on account of the grants made by the Department to individual workers.

Amongst grants to scientific societies are those to the Institution of Civil Engineers for the valuable work they have carried out on the deterioration of sea structures, to the Silk Association for the researches on the degumming of silk, to the Institution of Gas Engineers for the work of Dr. Mellor on Gas Retorts, to the Institution of Chemistry for their work on laboratory and optical glass, to the Pianoforte Manufacturers' Association for Dr. Clay's researches on sounding boards, to the British Fire Prevention Committee, to the Royal Society for Sir William Pope's researches on colour sensitiser dyes, and to the Manchester Association of Engineers for Mr. Dempster Smith's researches on the hardening of tool steel.

Valuable work has been done for the Institution of Metals by Dr. Bengough and his colleagues on the corrosion of condenser tubes.

Grants have also been made to three educational institutions for work of urgent industrial importance: to the Stoke-on-Trent Central School of Science and Technology for researches on hard porcelain; to Sheffield University for work on glass technology; and to the Imperial College of Science and Technology for researches in technical optics. In the case of two of the industries concerned in the work aided at these educational institutions, research associations have been formed, while the negotiations with the third for the formation of a research association have reached an advanced stage.

VI.—*Developments during the Year 1919-20.*

The body of the Report itself gives a detailed account of the activities of the Department during the year 1919-20, and include reference to the development of research associations, the organisations of national research, the expansion of research in and for the Empire, aided research, patents, and the publications of learned societies.

ADDRESS TO THE
ENGINEERING SECTION OF THE
BRITISH ASSOCIATION.

By Professor C. F. JENKIN, C.B.E., M.A.,
President of the Section.

THE importance of research in all branches of industry is now becoming fully recognised. It is hardly necessary to point out the great possibilities of the Board of Scientific and Industrial Research,

formed just before the war, or to lay stress on the attention which has been called to the need for research by events during the war. Probably in no branch of the Services was more research work done than in the Air Service, and the advances made in all directions in connection with flying were astonishing. My own work was confined to problems connected with materials of construction, and as a result of that work I have come to the conclusion that the time has come when the fundamental data on which the engineering theories of the strength and suitability of materials are based require thorough overhauling and revision. I believe that the present is a favourable time for this work, but I think that attention needs to be drawn to it, lest research work is all diverted to the problems which attract more attention, owing to their being in the forefront of the advancing engineering knowledge, and lest the necessary drudgery is shirked in favour of the more exciting new discoveries.

It has been very remarkable how again and again in aeroplane engineering the problems to be solved have raised fundamental questions in the strength and properties of materials which had never been adequately solved. Some of these questions related to what may be termed theory, and some related to the physical properties of materials. I propose to-day to describe some of these problems, and to suggest the direction in which revision and extension of our fundamental theories and data are required and the lines on which research should be undertaken. Let us consider first one of the oldest materials of construction—timber. Timber was of prime importance in aircraft construction. The first peculiarity of this material which strikes us is that it is anisotropic. Its grain may be used to locate three principal axes—along the grain, radially across the grain, and tangentially across the grain. It is curious that there do not appear to be generally recognised terms for these three fundamental directions. A very few tests are sufficient to show that its strength is enormously greater along the grain than across it. How, then, is an engineer to calculate the strength of a wooden member? There is no theory, in a form available for the engineer, by which the strength of members made of an anisotropic material can be calculated.

I fancy I may be told that such a theory is not required—that experience shows that the ordinary theory is quite near enough. How utterly misleading such a statement is I will try to show by a few examples. Suppose a wooden tie or strut is cut from the tree obliquely so that the grain does not lie parallel to its length. In practice it is never possible to ensure that the grain is accurately parallel to the length of the member, and often the deviation is considerable. How much is the member weakened? This comparatively simple problem has been of immense importance in aeroplane construction, and, thanks to the researches made during the war, can be answered. The solution has thrown a flood of light on many failures which before were obscure. If the tensile strengths of a piece of timber are, say, 18,000 lb./sq. in. along the grain and 800 lb./sq. in. across it (radially or tangentially) and the shear strength is 900 lb./sq. in. along the grain—these figures correspond roughly with the strengths of silver spruce—then if a tensile stress be applied at any angle to the grain the components of that,

stress in the principal directions must not exceed the above strengths, or failure will occur. Thus we can draw curves limiting the stress at any angle to the grain, and similar curves may be drawn for compression stresses. These theoretical curves have been checked experimentally, and the results of the tests confirm them closely, except in one particular. The strengths at small inclination to the grain fall even faster than the theoretical curves would lead us to expect. The very rapid drop in strength for quite small deviations is most striking.

Similar curves have been prepared for tensile and compressive stresses inclined in each of the three principal planes for spruce, ash, walnut, and mahogany, so that the strengths of these timbers to resist forces in any direction can now be estimated reasonably accurately.

As a second example consider the strength of plywood. Plywood is the name given to wood built up of several thicknesses glued together with the grain in alternate thicknesses running along and across the plank. The result of this crossing of the grain is that the plywood has roughly equal strength along and across the plank. Plywood is generally built up of thin veneers, which are cut from the log by slicing them off as the log revolves in a lathe.

Owing to the taper in the trunk of the tree and other irregularities in form, the grain in the veneer rarely runs parallel to the surface, but generally runs through the sheet at a more or less oblique angle. As a consequence, the strength of plywood is very variable, and tests show that it is not possible to rely on its having more than half the strength it would have if the grain in the veneers were not oblique. It is, therefore, obviously possible to improve the manufacture enormously by using veneers *split off*, following the grain, in place of the present sliced veneers. The superiority of split or riven wood over cut wood has been recognised for ages. I believe all ladders and ladder rungs are riven. Hurdles, hoops, and laths are other examples. Knees in ships are chosen so that the grain follows the required outline.

Owing to the enormous difference in strength in timber along and across the grain, it is obviously important to get the grain in exactly the right direction to bear the loads it has to carry. The most perfect example I ever saw of building up a plywood structure to support all the loads on it was the frame of the German Schutte-Lanz airship, which was made entirely of wood. At the complex junctions of the various girders and ties the wood, which was built up of very thin veneers—hardly thicker than plane shavings—layers were put on most ingeniously in the direction of every stress.

During the war I have had to reject numerous types of built-up struts intended for aeroplanes, because the grain of the wood was in the wrong direction to bear the load. The example shown—a McGruer strut—is one of the most elegant designs, using the grain correctly.

Many of the tests applied to timber are wrong in theory and consequently misleading. For example, the common method of determining Young's modulus for timber is to measure the elastic deflection of a beam loaded in the middle and to calculate the modulus by the ordinary

theory, neglecting the deflection due to shear, which is legitimate in isotropic materials; but in timber the shear modulus is very small—for example, in spruce it is only about one-sixtieth of Young's modulus—and consequently the shear deflection becomes quite appreciable, and the results obtained on test pieces of the common proportions lead to errors in the calculated Young's modulus of about 10 per cent.

The lantern plates show three standard tests; the first is supposed to give the shearing strength of the timber, but these test pieces fail by tension across the grain—not by shearing. Professor Robertson has shown that the true shear strength of spruce is about three times as great as the textbook figures, and has designed a test which gives fairly reliable results. The second figure represents a test intended to give the mean strength across the grain, but the concentration of stress at the grooves is so great that such test pieces fail under less than half the proper load. This fact was shown in a striking manner by narrowing a sample of this shape to half its width, when it actually bore a greater total load—i.e., more than double the stress borne by the original sample. The third figure represents a test piece intended to measure the rather vague quality, "strength to resist splitting." The results actually depend on the tensile strength across the grain, on the elastic constants, and on the accidental position of the bottom of the groove relatively to the spring or autumn wood in the annular rings. Unless the theory is understood, rational tests cannot be devised.

There are some valuable tropical timbers whose structure is far more complex than that of our ordinary northern woods. The grain in these timbers grows in alternating spirals—an arrangement which at first sight is almost incredible. The most striking example of this type of wood I have seen is the Indian "Poon." The sample on the table has been split in a series of tangential planes at varying distances from the centre of the tree, and it will be seen that the grain at one depth is growing in a right-hand spiral round the trunk; a little farther out it grows straight up the trunk; further out it grows in a left-hand spiral, and this is repeated again and again, with a pitch of about two inches. The timber is strong and probably well adapted for use in large pieces—it somewhat resembles plywood—but it is doubtful whether it is safe in small pieces. No theory is yet available for estimating its strength, and very elaborate tests would be needed to determine its reliability in all positions. I had to reject it for aeroplanes during the war for want of accurate knowledge of its properties.

These examples show how necessary it is to have a theory for the strength of anisotropic materials before we can either understand the causes of their failure or make full use of their properties or even test the rationally.

The second material we shall consider is steel, and in dealing with it I do not wish to enter into any of the dozen or so burning questions which are so familiar to all metallurgists and engineers, but to call your attention to a few more fundamental questions. Steel is not strictly isotropic—but we may consider it to be so to-day. The first obvious question the engineer has to answer is, "What is its strength?" The usual tests give the

Ultimate Strength, Yield Point, Elastic Limit, the Elongation, the Reduction of Area, and perhaps the Brinell and Izod figures. On which of these figures is the dimension of an engine part, which is being designed, to be based? If we choose the Ultimate Strength we must divide it by a large factor of safety—a factor of ignorance. If we choose the Yield Point we must remember that none of the higher-grade steels have any Yield Point, and the nominal Yield Point depends on the fancy of the tester. This entirely imaginary point cannot be used for accurate calculation except in a very few special cases. Can we base our calculation on the Elongation—the Reduction of Area—the Izod test? If we face the question honestly we realise that there is no known connection between the test results and the stress we can safely call on the steel to bear. The only connecting link is that cloak for our ignorance—the factor of safety.

I feel confident that the only reliable property on which to base the strength of any engine part is the suitable *Fatigue Limit*. We have not yet reached the position of being able to specify this figure, but a considerable number of tests show that in a wide range of steels (though there are some unexplained exceptions) the Fatigue Limit for equal \pm stresses is a little under half the Ultimate Strength, and is independent of the Elastic Limit and nominal Yield Point, so that the Ultimate Strength may be replaced as the most reliable guide to true strength, with a factor—no longer of ignorance, but to give the fatigue limit—of a little over 2.

If the Fatigue Limit is accepted as the only sound basis for strength calculation for engine parts, and it is difficult to find any valid objection to it, then it is obvious that there is urgent need for extensive researches in fatigue, for the available data are most meagre. The work is laborious, for there is not one Fatigue Limit, but a continuous series, as the signs and magnitudes of the stresses change. Many problems in connection with fatigue are of great importance and need much fuller investigation than they have so far received—e.g., the effect of speed of testing; the effect of rest and heat treatment in restoring fatigued material; the effect of previous testing at higher or lower stresses on the apparent fatigue limit of a test piece. Some observers have found indications that the material may possibly be strengthened by subjecting it to an alternating stress below its fatigue limit, so that the results of fatigue tests may depend on whether the limit is approached by increasing the stress or by decreasing it.

Improved methods of testing are also needed—particularly methods which will give the results quickly. Stromeyer's method of measuring the first rise of temperature, which indicates that the fatigue limit is passed, as the alternating load is gradually increased, is most promising; it certainly will not give the true fatigue limit in all cases, for it has been shown by Bairstow that with some ranges of stress a finite extension occurs at the beginning of a test and then ceases, under stresses lower than the fatigue limit. But the fatigue limit in that case would not be a safe guide, for finite changes of shape are not permissible in most machines, so that in that case also Stromeyer's test may be exactly what is

wanted. It can probably be simplified in detail and made practicable for commercial use. Better methods of testing in torsion are also urgently needed, none of those at present used being free from serious defects. Finally, there is a fascinating field for physical research in investigating the internal mechanism of fatigue failure. Some most suggestive results have already been obtained, which extend the results obtained by Ewing.

For members of structures which are only subjected to steady loads I suggest that the safe stress might be defined by limiting the corresponding permanent set to a small amount—perhaps $\frac{1}{2}$ per cent or $\frac{1}{4}$ per cent. This principle has been tentatively adopted in some of the aircraft material specifications by specifying a Proof Load which must be sustained without a permanent extension of more than $\frac{1}{2}$ per cent. Whether this principle is suitable for all materials and how it will answer in practice remains to be proved by experience. It is at any rate a possible rational basis for determining the useful strength of a material under steady loads.

The relation between the proof stress and the shape of the stress-strain diagram is shown in the lantern slide. The curve is the record of an actual test on a certain copper alloy. If a length A B corresponding to $\frac{1}{2}$ per cent elongation be set off along the base line and a line B P be drawn through the point B parallel to the elastic line, to cut the curve in P, then the stress at P is the stress which will give $\frac{1}{2}$ per cent permanent set. Though $\frac{1}{2}$ per cent may appear rather a large permanent set to allow it will be seen from the figure that it is less than the elastic elongation would have been at the same stress, and we do not usually find elastic elongations serious.

As a commercial test the proof load is very easily applied. For this alloy the specified proof load is shown by the horizontal line so labelled. This load is to be applied and released, and the permanent extension is required by the specification to be less than $\frac{1}{2}$ per cent. This sample passes the test easily. On the figure the condition for complying with the specification is that the curve shall fall above Q. But the test does not require the curve to be determined.

(To be continued.)

THE VOLUMETRIC METHODS FOR ESTIMATING TIN.

By J. G. F. DRUCE, M.Sc., A.I.C.

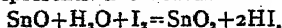
IN the course of certain investigations on the double chlorides of tin it has been necessary to carry out many quantitative analyses for tin. Frequently the metal was estimated by a gravimetric process. In those cases where the tin was present in the stannous condition it was possible to estimate it by volumetric methods.

A number of these processes have been tried in a systematic examination to find out the most suitable. Most volumetric methods were found to be satisfactory but it may not be generally realised that stannous tin can be most easily and accurately determined in acid solutions.

The results obtained with the various oxidising solutions are given below. Potassium stannochloride $K_2SnCl_6 \cdot 2H_2O$ was chosen as the most

suitable compound of stannous tin for preparing the standard solutions. It is easily obtained in the form of pure, stable crystals, which dissolve readily in dilute mineral acids.

Lenßen (*J. pr. Chem.*, 1859, lxxviii., 193) titrated stannous oxide dissolved in alkali with a standard iodine solution. The alkaline tin solution was obtained by dissolving the tin salt in sodium tartrate solution and adding excess of sodium carbonate solution. The following equation represents this reaction:—



Muller (*Bull. Soc. Chim.*, 1900, xxv., 1002), modified the method by dissolving the substance in hydrochloric acid, and then added Rochelle salt together with sodium carbonate.

For this method, 5.174 grms. of potassium stannochloride were dissolved in 50 cc. of dilute hydrochloric acid (one volume of concentrated acid to three of water). The solution was made up to 250 cc. with water containing one per cent of sodium carbonate dissolved in it in order to minimise oxidation caused by the presence of air. For each titration, 10 cc. of this solution (0.1008 normal) were mixed with an equal volume of a saturated solution of Rochelle salt, and finally 25 cc. of a saturated sodium bicarbonate solution were added. The solution was then alkaline to litmus, and was titrated with a decinormal solution of iodine, a little starch paste being added as indicator towards the end of the titration. Warming was quite unnecessary. It will be observed that the results are a little low. Ten cc. of stannous solution required:—

Expt.	cc. I ₂ Soln	≡ gm. Sn.	Sn. present
1	9.65	0.05728	0.05984
2	9.55	0.05669	0.05984
3	9.60	0.05699	0.05984
4	9.55	0.05669	0.05984

Topf (*Zeitsch. anal. Chem.*, 1887, xxvi., 285) modified this method further by adding excess of iodine to the tin solution and titrating the excess with standard sodium thiosulphate solution. This seemed an unnecessary complication.

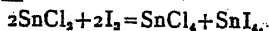
The following results were obtained using the above solutions and decinormal thiosulphate solution.

To 10 cc. of stannous solution, 20 cc. of iodine solution were added; the excess of iodine required:—

Expt.	cc. Na ₂ S ₂ O ₃	≡ gm. Sn.	Sn. present.
1	10.50	0.05626	0.05984
2	10.55	0.05609	0.05984
3	10.55	0.05609	0.05984
4	10.45	0.05669	0.05984

Estimation of tin by titrating stannous solutions with standard iodine solution in the presence of hydrochloric acid has been successfully employed by S. W. Young (*J. Amer. Chem. Soc.*, 1897, xix., 515 and 807), and by Ibbotson and Brearley (*CHEMICAL NEWS*, 1901, lxxxiv., 167) who obtained very satisfactory results.

The hydrochloric acid solution of the tin salt was titrated with standard iodine solution until the end point was almost reached, when a little starch paste was added. The following reaction took place:—



In order to obtain a paste which would give a

"homogeneous" appearance to the blue-black starch iodide, the starch (5 grms.) was first ground in a mortar with 10 cc. of water and then poured into 200 cc. of boiling water, and ebullition continued for five minutes.

10 cc. of the above potassium stannochloride solution required:—

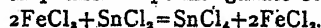
Expt.	cc. I ₂	≡ Grms. Sn.	Sn. present.
1	9.80	0.05817	0.05984
2	9.85	0.05847	0.05984
3	9.85	0.05847	0.05984

Using a fresh solution containing 20.84 grms. K₂SnCl₆·2H₂O per litre (i.e., 0.1012 normal).

Expt.	cc. I ₂	≡ Grms. Sn.	Sn. present.
4	10.15	0.06024	0.06009
5	10.10	0.06009	0.06009
6	10.05	0.05965	0.06009

This seemed to be the most convenient process for estimating tin by volumetric means. It gave satisfactory results for stannous chloride, the inorganic stannochlorides (*CHEMICAL NEWS*, 1918, cxvii., 193), and the stannochlorides of the aliphatic amines (*ibid.*, 1919, cxviii., 1), but was less suitable for most of the aromatic amine compounds owing to the tendency of solutions of these to darken during the titration and thus obscure the end point.

Lowenthal (*J. pr. Chem.*, 1858, lxxvi., 484) has described a method whereby stannous chloride was treated with excess of ferric chloride, which becomes reduced to ferrous chloride, which was titrated with potassium permanganate solution.



His method has now been repeated but the results are not so good as those above. It is not very reliable since the end point is somewhat uncertain.

Using decinormal potassium permanganate solution, 10 cc. of the second tin solution required:—

Expt.	cc. KMnO ₄	≡ gm. Sn.	Sn. present.
1	9.05	0.05359	0.06009
2	8.10	0.04749	0.06009
3	8.80	0.05224	0.06009
4	9.15	0.05401	0.06009
5	7.40	0.04392	0.06009

A satisfactory method of estimating tin by means of permanganate has, however, been devised in which the hydrochloric acid present during titration was kept at a minimum by dissolving the stannous salt in dilute sulphuric acid and titrating the solution as soon as possible after it had been prepared.

The end point was quite sharp and the results were good as the following shows.

5.205 grms. potassium stannochloride were dissolved in 50 cc. of dilute sulphuric acid, and the solution was made up to 250 cc., with one per cent sodium carbonate solution. 10 per cent of this solution then required:—

Expt.	cc. KMnO ₄	≡ gm. Sn.	Sn. present.
1	10.15	0.06024	0.06003
2	10.00	0.05935	0.06003
3	10.10	0.06009	0.06003
4	10.05	0.05965	0.06003

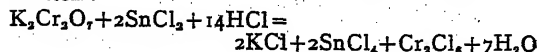
As a rule, titrations with potassium dichromate solutions were not found to be reliable for the estimation of tin. Reynolds (*CHEMICAL NEWS*, 1908, xcvi., 13) described a special indicator for use in this process which gave fairly good results. It was obtained by heating azobenzene with strong

sulphuric acid until a violent reaction began. The product was poured into water and gave a reddish solution decolourised by stannous chloride, but restored by potassium dichromate.

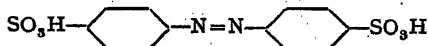
Using decinormal $K_2Cr_2O_7$, 10 cc. of potassium stannochloride, 0.1012 normal, required:—

Expt.	cc. $K_2Cr_2O_7$	≡ grm. Sn.	Sn. present
1	10.35	0.06143	0.06009
2	10.20	0.06054	0.06009
3	10.20	0.06054	0.06009
4	10.25	0.06084	0.06009

The equation expressing the oxidation of stannous chloride with potassium dichromate may be written:—



Stannous chloride was found to act upon the indicator to produce sulphanilic acid stannichloride ($NH_2.C_6H_4.SO_3H$), H_2SnCl_4 (see CHEMICAL NEWS, 1919, cxix., 74), when heated for some time in dilute hydrochloric acid. The salt began to darken at about 265–270° C., and it yielded sulphanilic acid after the removal of tin as sulphide. Hence the indicator is probably azobenzene- $\beta\beta'$ -disulphuric acid,



Summary.

The volumetric methods for estimating tin have been examined. The metal can be readily determined in acid solution by means of standard iodine solutions. Titration with potassium permanganate gave satisfactory results in the presence of sulphuric acid.

PERMEABILITY OF RUBBER TO GASES.

By J. D. EDWARDS and S. F. PICKERING.

[ABSTRACT.]

CERTAIN of the factors which determine the permeability of rubber to gases have been investigated and the relative rates of penetration of a number of gases determined. The major findings may be summarised as follows:

1. The permeability of rubber compounds varies with the composition as would be expected. The aging of rubber films is accompanied by a decrease in permeability. A similar decrease may be affected by over-vulcanisation. The rubber which shows a very low permeability for these reasons is usually very much deteriorated and frequently brittle so that it is a disadvantage from the standpoint of gas lighters.

2. The permeability to any gas is found to be directly proportional to its partial pressure provided the total pressure is constant. The variation of permeability with total pressure depends on the thickness of the rubber, the way in which it is supported, &c.

3. The permeability to hydrogen is inversely proportional to the thickness of the rubber. No other gas was tested in this respect.

4. The specific permeability to hydrogen at 25° C. of vulcanised rubber similar to the grade known as dental dam is about 20×10^{-6} cc. per minute. This value varies somewhat with the age and chemical characteristics of the rubber.

5. The temperature coefficient of permeability is quite high. For example, in the tests at 100° C., the permeability to carbon dioxide or helium was about 17 times the rate at 0° C.; the permeability to hydrogen was about 22 times as great at 100° as at 0° C.

6. The relative permeability of rubber to some common gases is shown in the following summary:

Gas	Relative Permeability Hydrogen=1
Nitrogen	0.16
Air	0.22
Argon	0.26
Oxygen	0.45
Helium	0.65
Hydrogen	1.00
Carbon Dioxide	2.90
Ammonia	8.00
Methyl chloride	18.50
Ethyl chloride	200.00

7. The permeability of rubber to water vapour is high—approximating 50 times the permeability to hydrogen. The value not having been determined with any precision is not included in the table above.—*Journ. Franklin Inst.*, August, 1920.

MINERAL RESOURCES OF THE WORLD.

Magnesite.*

* Pamphlet issued by the Imperial Mineral Resources Bureau, entitled "The Mineral Industry of the British Empire and Foreign Countries."

Magnesite is essentially magnesium carbonate; it may be spathic and comparatively coarse in its crystallisation, containing a considerable percentage of ferrous carbonate, or it may be chalk-like compact, or crypto crystalline in texture.

Magnesite is widely distributed over the surface of the earth. Austrian magnesite is spathic, and contains ferrous carbonate, and is known as breunnerite. Chalk-like magnesite, which is the commercially important, occurs in India, Australia, Greece, Italy, and California. Another variety of magnesium carbonate, hydromagnesite, is a distinct mineral species, with a chemical composition and physical properties essentially different from those of magnesite. Deposits are found in British Columbia and Spain.

Table I. gives the approximate analyses of different forms of magnesite.

TABLE I.

	Spathic Breun- nerite Austria. per cent.	Spathic Magnesite of Quebec, Norway and Washington per cent.	Compact Magnesite of Greece, India and California per cent.	Hydro- magnesite of Atlin, British Columbia. per cent.
Magnesia	38.44	38.47	47	42
Lime	1.3	0.10	0.2	0.2
Iron Oxide and Alumina	2.7	2	1	1
Silica	1.5	1.3	1.3	1
Carbon Dioxide	50	49.51	50	36
Water	—	—	—	19

Magnesite is utilised chiefly as a source of magnesia, which is obtained from it by calcination in kilns: (1) When heated to a temperature not

TABLE II.—*World's Production of Raw Magnesite.*

	1913	1914	1915	1916	1917	1918	1919
Union of South Africa ...	403	519	569	553	709	756	929
Canada ...	nil	nil	14,778	48,980	58,076	46,480	9,020
India ...	14,462	1,707	7,572	17,928	18,499	5,949	—
Australia ...	7,220	2,056	1,720	4,121	9,588	4,203	9,772
Austria-Hungary ...	200,947	133,099	36,541	38,527	48,622	—	—
Greece ...	118,054	136,701	159,981	199,484	162,938	39,340	—
Italy ...	600	1,140	9,200	18,252	31,070	28,882	—
Spain ...	958	583	1,400	2,500	800	1,700	—
United States ...	8,740	10,248	27,676	140,630	287,512	210,168	147,005

exceeding 1000° C., it is known as caustic magnesite, and is used in conjunction with magnesium chloride for the manufacture of oxychloride cements. (2) When heated to a high temperature (over 1500° C.), the product is known as dead-burnt or sintered magnesite and is used for a variety of purposes, principally as a refractory lining for furnaces, and for making refractory blocks, crucibles, and tweres. Other uses include its conversion into magnesium bisulphite, for use in the manufacture of paper from wood pulp; in the manufacture of carbon dioxide, and for medicinal and chemical use in the form of magnesium sulphate.

The pamphlet gives a table giving the world's production of raw magnesite, which is reproduced (Table II.). In addition to the countries mentioned in this table, Cyprus, Norway, Serbia, Russia, Mexico, and Venezuela have produced magnesite. The Cyprus output in 1916 was 15 tons. Figures for Norway are not available. Russia's pre-war annual production of raw magnesite is estimated at 15,000 to 20,000 tons. Venezuela exported 6360 and 1700 metric tons of magnesite in 1916 and 1917 respectively.

PROCEEDINGS OF SOCIETIES.

ROYAL PHOTOGRAPHIC SOCIETY OF GREAT BRITAIN.

Sixty-fifth Annual Exhibition—1920.

THE experiment made four years ago by the Royal Photographic Society of Great Britain of holding its Annual Exhibition, free to the public, at its home at 35, Russell Square, proved so successful that it has been continued, and the public are again invited to view the Exhibition free of charge.

The present is the Sixty-fifth Annual Exhibition, and many changes in the character of the photographs shown, and the materials employed, have taken place since Her Majesty Queen Victoria and Her Royal Consort honoured the Society by attending the first of these gatherings. During the late War, photographs on view were of necessity mainly produced by home workers, but now that some approach to normal peace conditions is taking place, the Society's Exhibition is once again of international character. The United States and Canada have entered large numbers of prints of admirable quality, all the more

worthy of careful study, because there is, as might be expected, a subtle difference in aim and accomplishment. The Continental nations, as they are still suffering from the effects of the war, are not so strongly represented, but it may be hoped that another year will enable them once again to take the position they previously held.

The exhibits are, as is customary, divided into Pictorial, Colour (including transparencies) and Scientific Sections; the first being in the Meeting Room on the first floor, the others in the Council and Committee Rooms on the second floor, and a special section exemplifying recent improvements in the methods of applying radiographic materials is in the Library on the ground floor.

It is impossible, in the course of a brief review, to deal with the exhibits in detail, but it will be seen on entering the Pictorial Section that a strong selection of portraiture is placed along the upper part of the walls about a third of the way round, and culminates in a life-like and expressive portrait of the President of the Society, Dr. G. H. Rodman. Beneath these portraits, the arrangement includes figure studies, architectural subjects, and pure landscape. The same happy interchange of subject continues around the walls, and the section is far and away the strongest in numbers and quality that we have seen during the last six years.

Proceeding to the Council Room, the visitors will be struck by a series of four lunar photographs by the Mount Wilson Observatory (California). These are, it is stated by astronomical experts, to be the finest of their kind that have been produced. The crispness of detail in the craters and prominences, obtained by means of the 100-inch reflector telescope, are indeed remarkable. From our own Greenwich Observatory are contributed by the Astronomer Royal, photographs of the total eclipse of the sun in 1919, illustrations of the great sun spot, 1920, and a photograph of the new star Cygnus, taken on August 22nd, 1920, with the 30 inch reflector.

Among the numerous radiographic exhibits is a fine set by Dr. Robert Knox. This set deals with the use of X-rays in the diagnosis of diseases. The Sunic Research Laboratory has entered a set of prints illustrating the application of the Röntgen processes in metallography, disclosing faults in welds, &c.

A set of low power photomicrographs of the eggs of British butterflies has secured a medal for Mr. Alfred E. Tonge. Other work by such well-known naturalists as Hugh Main and F. Martin-Duncan call for attention, and many visitors will be interested in the beautiful photo-radiographs

by Arthur C. Banfield, and also in a fine series of photomicrographs of coal plant fossils, by the President.

On the same floor is the Colour Section. The colour transparencies are not quite so numerous as in past years, but average larger in size, and are quite up to the standard in technical excellence. Medals have been awarded in this section to D. Mischol (a Swiss worker), and to R. G. Wheeler Bush. There is nothing new in the way of colour prints, but two or three by well-known processes are shown by A. del Solar Dorrego and John Bean.

In the same room are several exhibits sent by the Research Laboratory of the Eastman Kodak Co., of Rochester, New York, including photographs of sensitometric apparatus, and of colour co-efficients.

In one of the Library Rooms on the ground floor is installed a number of viewing boxes for the display of X-ray negatives produced on Eastman duplicated films, by N. E. Luboshez, who has been employing several superimposed films, each film receiving special treatment in exposure and development. By printing through several films selected according to the purpose for which they are required, placing them in contact and printing from them, results are obtained which could not be got from a single film, and which show a distinct advance in radiographic technique and definition. For his work in this direction the Society's medal has been awarded to Mr. Luboshez.

CORRESPONDENCE.

SODIUM PHOSPHIDE—METALLIC HYDRIDES.

To the Editor of the Chemical News.

SIR,—Since the preliminary account of sodium phosphide was published (CHEMICAL NEWS, cxxi, 104), we have found that we have overlooked a series of papers published in *Comptes Rendus*. Hugot (*Compt. Rend.*, 1895, cxxi, 206; 1898, cxxvi, 1719) prepared a red compound, $\text{Na}_3\text{H}_2\text{P}_2$, by the action of red phosphorus on sodium in liquid ammonia, which evolved PH_3 with acids and water. This was obviously not the compound we obtained by direct union of the elements, as we obtained it as a greyish to white mass. Joannis (*Ibid.*, 1894, cxix, 557) states that PH_3 in presence of liquid ammonia reacts with sodium to form NaH_2P , which is converted by heat into Na_3P , the latter yielding PH_3 with cold water. An unstable phosphide, Na_2P_2 , is said to be formed when sodium and phosphorus are heated together for several days in vacuo at 450° (Hackspill and Bossuet, *Compt. Rendus*, 1912, cliv., 209). At the ordinary temperature, we found phosphine to react with sodium, producing sodium phosphide, probably the Na_3P described by Joannis (*Loc. cit.*). We have since prepared the phosphide in a variety of ways, which will be described in a further communication.

Uses of Metallic Hydrides.—Corrigan (CHEMICAL NEWS, cxix, 275) states that the uses of the metallic hydrides are practically nil. This appears

to be incorrect; e.g., Kaiser originated a method of manufacturing ammonia by the use of CaH_2 (French Patent, No. 350,966; c.f. Haber and Oordt, *Zeit. anorg. chem.*, 1905, xliii, 111; xlv., 341). The hydride is converted into nitride by passing a stream of hydrogen over the heated compound. When the nitride is heated in a current of hydrogen, ammonia is liberated

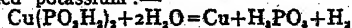
1. $\text{Ca} + \text{H}_2 = \text{CaH}_2$.
2. $3\text{CaH}_2 + 2\text{N}_2 = \text{Ca}_3\text{N}_2 + 2\text{NH}_3$.
3. $\text{Ca}_3\text{N}_2 + 6\text{H}_2 = 3\text{CaH}_2 + 2\text{NH}_3$.

The action seems to go on the same whether the gases are passed into the tube together or separately. J. Lipski (*Zeit. Elektrochem.*, xv., 189-206) proposed to use cerium hydride, CeH_3 , for the same purpose. The latter was heated in a current of nitrogen, and in 3½ hours 50 per cent theoretical yield of NH_3 was produced. The dessicated product did not give such a rapid reaction (probably due to surface oxidation—active CeH_3 gradually becomes inactive in a current of H_2 unless the latter is carefully purified from O_2). The dissociation of CeH_3 becomes considerable at moderate temperature. The reaction corresponds to the equation $\text{CeH}_3 + \text{N}_2 = \text{CeN} + \text{NH}_3$. The hydride from impure materials is stated to have given good results.

Cuprous Hydride, Cu_2H_2 .—Corrigan states (CHEMICAL NEWS, 1919, cxix., 274) that this is obtained by the action of CuSO_4 on hypophosphites. Bourgault (*Compt. Rend.*, cxlviii., 415-17), however, showed that with excess of CuSO_4 , a brownish-yellow precipitate is produced, of CuH_2PO_3 , which gave on boiling Cu and the cupric salt. Bourgault also states that when NaH_2PO_3 is in excess, Cu_2H_2 is produced. This latter, on boiling with NaH_2PO_3 solution, evolves hydrogen, and reduces the hypophosphite to phosphate and phosphite. Copper produced from CuSO_4 by Zn shows this effect, but to a much lesser extent.

Copper hypophosphite may be prepared by the action of CuSO_4 on barium hypophosphite. The solution is filtered, and is precipitated by alcohol in crystalline form.

The solution is decomposed by addition of precipitated potassium:—



no copper hydride being formed. Copper hypophosphite, in the absence of Pd , is decomposed differently by heat, Cu_2H_2 being first formed, and then metallic copper, phosphorous and hypophosphorous acids (Engel, *Compt. Rendus*, Oct. 12, 1899).—I am, &c.,

E. TOMKINSON.

Barrow-in-Furness, September 23, 1920.

THE SOCIETY OF LEATHER TRADES CHEMISTS.

To the Editor of the Chemical News.

SIR,—A Meeting of the British Section of the S.L.T.C. will be held at the Leather Industries Department, The University, Leeds, on Saturday, October 16, 1920, at 10.30 a.m. The agenda is as follows:—

Report from Hide Powder Committee.

Reports from Analysis Committees.

"Limeyard Control," by Mr. F. C. Thompson.

"Sulphonated Oils," by Mr. C. F. Barber.

"Tannin Analysis," by Mr. G. E. Knowles.
 "Chrome Leather Analysis," by Mr. R. F. Innes.
 "Dressing Leather Analysis," by Mr. P. R. Barker.
 "Sole Leather Analysis," by Dr. J. Gordon Parker.
 Leather Analysis—Water Soluble Matters.
 Mutual Membership Scheme.
 I am, &c.,
 STANLEY HIRST, Hon. Sec. British Section.

NOTES.

GALLANT CONDUCT TO BE REWARDED.—The Lord Mayor of Leeds will shortly present the Gallant Conduct Award of the British Industrial "Safety First" Association to James H. Tebbs, a worker at Messrs. Brotherton's Ammonia Distillery at Leeds, for his plucky rescue of a fellow workman. A. L. Pilkington, a fitter employed at Messrs. Brotherton's works, was repairing the top of an upright boiler used as a decomposer, when he was badly gassed and lost consciousness. He fell face forward on to the top of the boiler. Tebbs was passing at the time, and noticed something wrong with Pilkington. Without hesitation, he climbed the ladder which Pilkington had been using and got over his recumbent body. This was an extremely risky proceeding, as the top of the boiler was only five feet in diameter. Tebbs lifted Pilkington's head away from the gas, tied a rope round his body and lowered the unconscious man to the ground. He was then conveyed to Leeds Infirmary. This award for gallant conduct is but one of the ways in which the British Industrial "Safety First" Association seeks to encourage workers in taking steps for practical safety. It gives an additional interest to the forthcoming Accident Prevention Congress at Olympia on the 22nd instant, under the joint auspices of the Home Office and the British Industrial "Safety First" Association, at which the Home Secretary and Lord Leverhulme will preside, and papers will be read by members of the Home Office staff and by representatives of several firms which have proved the worth of "Safety First."

TECHNICAL COLLEGE, BRADFORD.—The Calendar of the Bradford Technical College has recently been issued and contains full details of the courses of instruction in the various departments of the College. The College, which was established in 1877, provides full-time (day) courses and part-time (mainly evening) courses in its main departments of Textile Industries, Chemistry, Dyeing, Mechanical, Civil, and Electrical Engineering, and Biology. The full-time courses extend over three or four years and lead to the Diploma of the College, and the part-time courses, which involve attendance on three evenings a week during three or five sessions, lead to Senior and Advanced Course Certificates of the College. The courses have been specially designed to meet the needs of students wishing to receive a technological training which will enable them to occupy the higher positions in industry. The full-time courses in the College are of University standard, and candidates for admission to these courses, who have not passed the Matriculation examination or one of its equivalent examinations, are required to

pass the College Entrance Examination, the standard of which is approximately the same as that of the Matriculation examination. Special consideration is, however, given to the cases of students who have been in whole time industrial employment for several years, and who may wish to enter one of the full-time courses. The part-time (evening) courses in the College are intended to meet the needs of those students who are engaged in industry during the greater part of their time. These courses form a large and important part of the work of the College. Many of the advanced courses are attended by those students who have already completed systematic technological courses, and have entered industry but who wish to keep abreast with the various developments which are continually taking place. In addition to the organised courses, the College also provides special facilities for those students who may wish to undertake advanced study. Students may also undertake research in the various departments of the College, and, with a view to the further development of this part of the work of the College, additional equipment and accommodation is being provided. The equipment of the College is extensive and includes a complete plant for the washing, carding, combing, spinning, weaving, dyeing, and finishing of textiles. A special feature of the equipment is the Power House, which has been arranged for demonstration purposes and which supplies the whole of the power and light required by the College. Mention should also be made of the Engineering Laboratories, which include special Mechanics, Material Testing, Heat Engine, Motor Car and Electrical Laboratories.

NOTE ON ALUMINIUM.—E. Rattenbury Hodges.—It can hardly have escaped observation that aluminium is slowly acted upon by strong acetic acid. Most works on chemistry which I have consulted make no reference to this, but Watt's Dictionary (vol. i., p. 142, col. 2) states, under "Reactions"—"6. Most carbon acids, e.g., acetic, tartaric, have little or no action on Al; but in presence of NaClAq, the action becomes marked," &c. After exposing some foil of the metal to the action of strong acetic acid for a week or ten days, I noted that some alumina was precipitated. The clear supernatant fluid answered the usual tests, the solution being aluminium acetate. This, by slow evaporation in the air (at 60° F.), yields a rather stiff colloid mass which is colourless and transparent; the dry film shows lines of fracture in all directions.

COLLOIDAL PHYSICS AND CHEMISTRY.—The forthcoming General Discussion on the "The Physics and Chemistry of Colloids and their Bearing on Industrial Questions" which is being arranged jointly by the Faraday Society and the Physical Society of London has been fixed to take place on Monday, October 25 next, at the Institution of Mechanical Engineers, Storey's Gate, London, S.W.1. The Discussion will be presided over by Prof. Sir W. H. Bragg, K.B.E., F.R.S., and it will be introduced by Prof. Dr. The Svedberg, of the University of Upsala, who will give a general survey of the subject before discussion is opened in its various branches. Non-members of the above Societies desirous of attending the Discussion may obtain tickets of admission from Mr. F. S. Spiers, 10, Essex Street, London, W.C.2.

GLASGOW BRITISH INDUSTRIES FAIR.—Applications for space in the forthcoming Fair to be held in the Kelvin Hall, Kelvingrove, in the spring of next year, are coming forward in large numbers. Exhibitors at the former shows are already well forward, while many important firms not formerly represented are enquiring for space. This is particularly so in the textile section, which was one of the features of the Fair held in the spring of the present year. Many new firms will be represented, and this should add to the success of the Exhibition. The fact that the Kelvin Hall has been extended, making it the largest building in the country specially erected for exhibition purposes, gives the promoters of the show—the Glasgow Corporation with the support of the Board of Trade—every opportunity to accommodate a larger number of exhibitors than formerly.

ROAD TRANSPORT PROGRESS.—The Society of Motor Traders and Manufacturers are arranging to open an extensive Exhibition at Olympia on October 15. Great advances are being made in motor traction, and it is becoming increasingly evident that the lorry will be a serious rival of the railway. The Exhibition will close on the 23rd of this month, which seems a very short time for a subject of such importance.

ROYAL PHOTOGRAPHIC SOCIETY.—The Annual Exhibition will remain open until October 30, at the Rooms of the Society, 35, Russell Square. No charge is made for admission. Interesting lectures are given on Tuesday and Friday evenings. Under the Presidency of Dr. G. H. Rodman, the Scientific Section has been greatly developed, and a great many important exhibits are shown, including some fine radiographs by Dr. Robert Knox and others.

DISINFECTING FLUID.—The Metropolitan Borough of Poplar prepare and dispose of a large quantity of disinfecting fluid made by electrolyzing a solution of magnesium chloride, salt, and caustic soda. Over 33,000 gallons were made and used in 1919. The fluid appears to be giving great satisfaction.

The Secretary of the Department of Scientific and Industrial Research announces that a license, under Section 20 of the Companies (Consolidation) Act, 1908, has been issued by the Board of Trade to the British Cutlery Research Association, which has been approved by the Department as complying with the conditions laid down in the Government scheme for the encouragement of industrial research. The Secretary of this Association is Mr. J. M. Denton, P.O. Box 49, Sheffield.

THE BRITISH EMPIRE EXHIBITION.—The British Empire League, ever since its establishment in 1894, under the late Sir Robert Herbert, its first Chairman, has given whole-hearted support to exhibitions of British origin, as an effective aid to the development of the Empire, and on Nov. 12, 1918, the very day following the Armistice, the Committee unanimously resolved to further the holding of an Exhibition of Imperial industries in London at the earliest practicable date after the conclusion of Peace. When preliminaries had been sufficiently advanced, a luncheon was held at the British Empire Club, which was attended by official representatives

from every part of our Empire, including the Right Hon. W. M. Hughes, Prime Minister of Australia, the Right Hon. Sir Joseph Ward, then Treasurer of New Zealand, as well as our five High Commissioners for Canada, Australia, New Zealand, South Africa, and Newfoundland, all of whom urged the desirability of holding the proposed all-British Empire Exhibition. In face of the unanimity of the representatives of the Empire in favour of an Exhibition of British products and manufactures which would really be a commercial celebration of Peace, the Chairman wrote on behalf of the Committee to the President of the Board of Trade asking for the co-operation and financial assistance of His Majesty's Government, and the nomination of representatives to serve on a General Council for carrying out the project. His Majesty the King has graciously consented to be Patron, and His Royal Highness the Prince of Wales is President; and as has been announced, the Government has now decided to give the Exhibition all possible support, guaranteeing £100,000 subject to £500,000 being guaranteed by the commercial community. Already some of the principal banking, trading, and industrial concerns of the Empire have come forward as guarantors, and it is to be hoped that all the leading commercial houses will participate in the Guarantee Fund. After negotiations, a strong Executive Council and Administrative Committee have been formed, the following having been appointed as representatives of the British Empire League on both bodies: Sir George McLaren Brown, Sir John Cockburn, Mr. W. Herbert Daw, and Colonel Sir J. Norton-Griffiths, M.P., while the Chairman and Vice-Chairman of the League have been elected Vice-Presidents, and Mr. C. Freeman Murray, Secretary of the League, has been appointed Joint Hon. Secretary of the Guarantee Fund Committee of the Exhibition. The organisation having now been completed, there is every reason to believe that the Exhibition, which is to be held in 1923, will be a pronounced success. Everyone interested in the Unity of the British Empire will agree that a display in London of its vast resources in mineral wealth, food products, raw materials, and manufactured goods, must, as was pointed out by the late Duke of Devonshire, the first President of the British Empire League, result in "better commercial relations, by means of improved communications, by means of increased sympathy with each other, of increased knowledge of each other."—(Signed) Sydenham, (Chairman); Blyth (Vice-Chairman), British Empire League.

FAILURE OF METALS UNDER INTERNAL OR PROLONGED STRESS.—The Faraday Society, Institution of Mechanical Engineers, the Institute of Metals, and probably also the Iron and Steel Institute, contemplate holding early in 1921 a joint General Discussion on "The Failure of Metals under Internal or Prolonged Stress." While various aspects of the subject have already been discussed, some new matter will be placed at the disposal of the co-operating societies later in the year, and it is considered that this will afford an opportunity for a more comprehensive consideration of the subject than has yet been given to it. The problem to be discussed is the failure of metal articles as a result either of external

stresses to which they have been exposed for any length of time, or of internal stresses arising from conditions of manufacture, such as cold work, unequal expansion or contraction during casting and subsequent operations, including rapid heating and cooling. It is intended that the subject of the Discussion should include the phenomena known as "season cracking," "corrosion cracking," "fire cracking," and analogous forms of failure, and that iron and steel as well as non-ferrous metals should be dealt with. The scope of the discussion would permit of contributions relating to the properties and behaviour of materials other than metals which might throw light on the phenomena covered by the title. Anyone desirous of contributing to this discussion is asked to communicate with the Secretary of the Joint Committee, Mr. F. S. SPIERS, 10, Essex Street, London, W.C.2.

MEETINGS FOR THE WEEK.

Monday, October 11.

Biochemical Society, 5.

Wednesday October 13.

Conjoint Board of Scientific Societies, 3.

Thursday, October 14.

Institute of Chemistry (Liverpool Section).

Friday October 15.

Royal Society of Arts, 430. (Indian Section). "British Trade with India," by T. M. Ainscough.

Saturday, October 16.

Physiological Society, 4. (At Guy's Hospital).

NOTICES.

EDITORIAL.—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the Editor.

SUBSCRIPTIONS. £1 13s. per annum, payable in advance, should be addressed to the MANAGER.

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WANTED for the Library at the Ardeer Factory of Nobel's Explosives Co., Ltd., a well qualified Chemist having thorough knowledge of French and German. Applications, accompanied by details of experience, qualifications, etc., should be sent to the MANAGER, Research Section, Ardeer Factory, Stevenston, Ayrshire.

PATENTS, TRADE MARKS. Handbook and advice free—B. T. KING, British and U. S. Regd. Patent Attorney, 146a, Queen Victoria St., London. 35 years reference.

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3157.

EDITORIAL.

THE following papers have been received for publication, and will be inserted as soon as space permits:—

"A Modification of Skraup's Quinoline Synthesis."
By Edward de Bariv Barnett, B.S.c., F.I.C.
A convenient method of preparing quinoline in the laboratory is described in which ferric sulphate is employed as an oxidising agent. A catalytic modification of Skraup's process is also described.

"A New Form of Ozoniser for Laboratory Work."
By Y. V. Ramaiah and M. V. N. Swamy, B.A., Indian Institute of Science, Bangalore, India.

ANALYSIS OF DROPPINGS OF CATERPILLAR (*ANTHERAEA CYTHEREA*).

By Dr. CHARLES F. JURITZ, M.A., F.I.C.

A FEW months ago Mr. C. W. Mally, M.Sc., F.E.S., Government Entomologist for the Cape Province, handed me a parcel of caterpillar droppings from Uitvlugt, Cape Division, produced by larvæ of *Antheraea cytherea*. This caterpillar, Mr. Mally informs me, appears in great abundance on the wattle in early summer in certain years, when it completely strips the trees of leaves. In other years natural enemies cause it to disappear almost entirely. When abundant, the larvæ produce large quantities of droppings. The sample given me by Mr. Mally was analysed in this laboratory with the results stated below.

After ascertaining that the weight of 100 particles was 4.4310 grms., the whole of the sample submitted was crushed in a mortar and passed through a sieve with meshes of 1 mm. diameter; a portion of this sifted material was ignited at a low heat and produced a greyish white ash.

The following analytical figures were obtained, calculated in percentage of the sample as originally received:—

Water	11.10
Ash	11.06
Nitrogen	2.07
Potash	2.87
Lime	1.86
Phosphoric oxide	0.87

The proportion of moisture in the original sample is low and compares better with the general type of kraal manure (which ranges from 9 to 20 per cent) than with the usual type of horse, cow, or sheep manure (in which it may be said to vary between 66 and 86 per cent).

In order to compare the fairly dry unburnt manure, averages on a 10 per cent basis have been compiled in the following table, the figures for

the horse and cattle manure being taken from Aikman, "Manures and Manuring," 1894 edition, pp. 284, 286, and those for the kraal manure from my paper on the "Chemical composition of Karroo Ash" (Report S. A. Association for Adv of Science, 1915, p. 142).

	Horse Manure.	Cow Manure.	Kraal Manure.	Caterpillar Droppings
Water	10.00	10.00	10.00	10.00
Ash	14.51	16.88	40.47	11.20
Nitrogen	1.84	1.88	1.45	2.10
Potash	1.53	2.51	3.38	2.01
Lime	1.12	1.88	8.00	1.88
Phosphoric oxide	1.12	0.55	1.24	0.88

Taking, in each case, the amount of ash as 100, the following results have been calculated in percentages of the ash:—

	Horse Manure	Cow Manure	Kraal Manure	Caterpillar Droppings
Potash	10.54	14.87	8.35	25.05
Lime	7.72	11.14	19.77	16.82
Phosphoric oxide	7.72	3.26	3.06	7.86

The high percentage of potash in the droppings is no doubt due to the food of the caterpillar which, in this case, I understand, consisted of leaves of *Acacia cyclops* fed to them experimentally under cover, before collecting the sample, and I gather that under natural conditions they feed on the same species of wattle.

A quantity of leaves of *A. cyclops* was accordingly procured and analysed. The results, calculated in percentage of the fresh leaves, were as follows:—

Water	71.06
Ash	1.39
Nitrogen	1.07
Potash	0.25
Lime	0.13
Phosphoric oxide	0.12

As in the case of the caterpillar droppings, I have recalculated the above results on a 10 per cent water basis. The figures then appear as below:—

Water	10.00
Ash	4.46
Nitrogen	3.43
Potash	0.82
Lime	0.41
Phosphoric oxide	0.39

The inorganic constituents, calculated in percentages of the ash, are present in the following proportions:—

Potash	18.34
Lime	0.20
Phosphoric oxide	8.80

It will be noticed that, in the leaves, as in the droppings, potash is highest in amount of the three inorganic plant food constituents, and phosphoric oxide lowest; also that in the droppings these inorganic constituents, or, at all events, the potash and the lime, are present in a more concentrated form than in the acacia leaves.

The droppings were said to have been so abundant during the last season that it had been proposed to use them for fertilising purposes.

THE FIVE MAIN PRINCIPLES IN THE CONSTITUTION AND STRUCTURE OF THE CHEMICAL ELEMENTS.

By HAWKSWORTH COLLINS.

1. SINGLE chemical valences emanate from elements or portions (of elements) whose masses are 1, 3, 7, 23, and 39.

2. The non-metallic nature of an element is always due to a pair or pairs of electro-positive forces, each pair emanating from a portion of the element, of which the mass is 4, taking the mass of an atom of hydrogen as unit.

3. Monadic Na (23) takes a prominent part in the formation of all elements of greater mass than itself.

4. In the simpler elements H (1) forms the connecting link between the other portions 3, 7, 23, and 39. In the formation of the heavier elements, masses of 23 sometimes unite by forces which are not chemically evident without any intervening unit mass.

5. Each of the heavier elements is formed by the union of simpler elements (which are indicated in each case by mineralogical and chemical facts combined).

The first four principles have already been fully demonstrated, so that the following matter chiefly concerns the fifth.

There are nine pairs of elements connected by a mass of 90 (Table I.).

TABLE I.

Ru (101)	B (11)
Rh (102)	C (12)
Pd (106)	O (16)
Xe (130)	A (40)
Sn (118)	Si (28)
Ra (226)	Ba (136)
Os (191)	Ru (101)
Ir (192)	Rh (102)
Au (197)	Ag (107)

In six cases out of nine the heavier element happens to be in the same column of the Periodic Table as the lighter. There are nine columns, 0, 1, 2, 3, 4, 5, 6, 7, 8.

The probability that the heavier of a pair would accidentally be in the same column as the lighter is $1:4^5$, say $1:4$. *E.g.*, if the lighter is in the column 4, the heavier might be in 0, 2, 4, 6, or 8; or, if the lighter were in column 5, the heavier might be in 1, 3, 5, or 7.

Therefore, the probability that a pair would happen accidentally to be in the same column in six cases out of 9 is $1:49-3 \times \frac{1}{4} = 1:4^5 = 1:1024$. Therefore, the probability that this state of affairs is not due to accident is $1024:1$. But the probability against its being an accident is greatly increased (1) by the fact that Zr (90) is especially found intimately associated with most of these elements, and (2) by the fact that the difference of 90 in the atomic weights of four of the pairs of elements is due to something which produces no alteration in the atomic volume, and which, therefore, is in all probability the same thing in all the four cases. This will be demonstrated later.

The 46 integers in the last paper were obtained from only one set of data, viz., the two columns of experimental atomic weights, with the help of the Odd and Even Rule. No other consideration influenced them in the slightest.

From the integers so obtained it has been proved:—

1. That a mass of 23 with one valence takes a prominent part in the formation of the elements.

2. That a mass of 90 takes part in the formation of some elements which happen to be especially associated with Zr in mineralogy. Taking these two proofs into consideration, and also the three following statements (a), (b), and (c), the constitution and structure of 26 of the 46 heavier elements can be obtained.

(a) Mineralogical facts with regard to Na and Zr have only been mentioned as coincidences, and have taken no part in arriving at the above results (1 and 2), so that these facts are free for independent reasoning.

(b) Although the *maximum* valency of each element has been mentioned, it has not influenced the obtaining of the integer in any way. Only the differences of the valences of pairs of elements have been employed, and the observation as to whether the maximum valences were odd or even; so that the actual number representing the maximum valency of each element is free for independent reasoning with regard to each integer.

(c) The distinction between metallic and non-metallic valences has not been employed at all in arriving at the 46 integers, so that these are also free for independent reasoning.

Gallium (69) = Na_3 .

(a) The matrix of Ga is said to be: Si-Al-minerals from which most of the Na has been dissolved. This undoubtedly suggests that Ga has been formed from the extracted Na.

(b) The number 69 exactly explains the valency of Ga, one from each portion of 23.

(c) It also explains why Ga cannot act as a non-metal, for there is no free $\text{H}-\text{H}_3$.

(d) If it had not happened that when oxygen is taken as 16 some of the simple elements are whole numbers, the atomic weight of Ga would now be given as 69.6 ($\text{H}=1$).

(e) The integer obtained is especially suitable for explaining the mineralogical and chemical facts with regard to Ga; for there are no associated elements, the sum of whose atomic weights is equal to either of the two adjacent integers, and by means of which the valency of Ga can be explained.

(f) The probability that this particular number (obtained independently and not arbitrarily by means of the five proofs mentioned in the last paper) would be exactly equal to the sum of the atomic weights of intimately associated elements, and at the same time exactly explain the valency, and that neither of the two adjacent integers would be at all suitable for this purpose, is $1:3$ at least.

Remarks similar to *d*, *e*, and *f*, apply to all the following 25 elements and so will not be repeated.

Indium (115) = Na_2Ga .

(a) Indium is especially found with Ga.

(b) The number 115 exactly explains the valency.

(c) It also explains why In cannot act as a non-metal, for there is no free $\text{H}-\text{H}_3$.

Copper (63) = NaCa .

(a) In Siberia, Cu is associated with mesotype, an oxide of Na, Ca, Al, Si. Strings of Cu often reticulate through crystals of analcite and preh-

nite, which are oxides of Na, Ca, Al, Si. Native Cu is also especially associated with pectolite, an oxide of Na, Ca, Si.

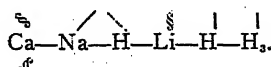
(b) The number 63 exactly explains why Cu sometimes acts as the monad Na and sometimes as the dyad Ca.

(c) It also explains why Cu cannot act as a non-metal.

Arsenic (75)=CuC.

(a) Arsenic is found especially associated with Cu. Domeykite, algodonite, and whitneyite are compounds of As and Cu. Tennantite, a common mineral, is a sulphide of Cu and As.

(b) By the Interrelationship of the Elements there are eleven pairs of elements, the sum of whose atomic weights is 75, and the sum of whose valences is always an odd number, 5, 7, or 9; so that a pentad could always be formed; but CuC is by far the most likely method of formation from the facts of mineralogy, and its structure would then be



(c) This formula also explains why As is non-metallic.

Silver (107)=AsS.

(a) Ag₂S is almost invariably found intimately associated with As₂S₃, and their molecular weights are equal, so that if each atom of As combined with one of S, the latter molecule would become Ag₂S by atomisation.

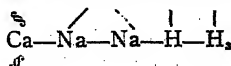
(b) The difference of the valences of As and S is one, so that the monad Ag could be formed by five pairs of valences becoming quiescent.

(c) Since there is only one valence there can be no free H—H₂, and therefore, by the theory Ag cannot be a non-metal.

Zirconium (90)=NaCaAl.

(a) Zr is found in astrophyllite with Na, Ca, Al; also in scapolite, a silicate of Na, Ca, Al; and in elaeolite, a silicate of Na, Ca, Al, K. The zircon-syenite or augite-syenite of Norway contains much elaeolite.

(b) Zr is a tetrad, and a tetrad could be formed from these three elements as follows:—



where the two valences from the Na portions are quiescent as they have been shown to be in several other cases.

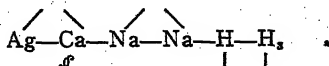
(c) This formula also explains the non-metallic nature of Zr.

Gold (197)=ZrAg.

(a) Silver always accompanies gold, and crystals of zircon are common in most auriferous sands.

(b) The monad Ag could combine with the tetrad Zr so as to form the triad Au, two of the valences becoming quiescent.

(c) The non-metallic nature of Au is explained by combining Ag with Zr in the following manner:—

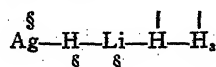


so that Au may also be said to be formed by the atomisation of Ag, Cu, and Al.

Antimony (119)=AgC.

(a) Native Sb is found in silver ores. Pyraargyrite, a common mineral, is a sulphide of Ag and Sb. Stephanite of similar composition is also an abundant ore of silver. Dyscrasite, a compound of Ag and Sb is found in silver mines, and is probably the ultimate matrix of Sb, as Dana says that pyraargyrite has been formed from it.

(b and c) The formula—



exactly explains the valency of Sb, showing why it is tribasic and diacidic.

Ruthenium (101)=Na₂Mn.

(a) Ru is found in iridosmine with platinum. This mineral occurs in situ in the Broken Hill district of New South Wales in a feldspathic rock. Feldspar contains Na with Si and Al, which together form Mn.

(b and c) The chemical compounds of Ru are exactly analogous to those of Mn, so that it is difficult to understand why the former is not put in a vacant place under Mn in the Periodic Table. The two valences from Na₂ are as usual quiescent.

Osmium (191)=ZrRu.

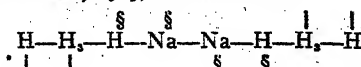
(a) Ru and Os are found together in auriferous sands, and crystals of zircon are very common in such sands.

(b and c) The valency of Os being similar to that of Ru is explained by the two non-metallic valences of Zr uniting with two of the metallic valences of Ru.

Iron (56)=Si.

(a) Native iron occurs in most meteorites as a spongy cellular matrix in which are embedded grains of chrysolite or other silicates.

(b and c) The position of Fe in the Periodic Table indicates that it may be an octad, in which case its constitution and structure would conform with those of the first 25 elements (CHEMICAL NEWS, Dec. 26, 1919) and would be—



But, since its valency is observed to be hexadic, if the valences of the two Na-ports were quiescent as usual, its valency (dibasic and tetracidic) would be exactly explained.

As this element is distinguished by its magnetic character, it would be expected that either its constitution or its structure or both would be distinguishable in some way from other elements. These requirements are satisfied, as (1) it is the only non-metallic element whose structure can be written down (in accordance with this theory) symmetrically; (2) it is the first element (in the order of ascending atomic weight) whose experimental atomic weight is more than 0.1 below the nearest integer; and this is probably due in some way to its magnetic property. The symmetry of the atom would obviously enable it to lie in a magnetic field in a way that is possible for no other atom.

Rhodium (102)=Na₂Fe.

(a) Rh and Fe partially replace Ir in osmiridium. Ir, Rh, and Fe also occur together in nefdanskite and sisserskite.

(*b* and *c*) Rh seems to be analogous to Fe in valency according to the Periodic Table.

Iridium (192) = $ZrRh$.

(*a*) Ir and Rh are found together in auriferous sands, and crystals of zircon are very common in such sands.

(*b* and *c*) Ir is recognised as being a similar element to Rh.

Iodine (127) = Na_4Cl .

(*a*) The evidence of mineralogy is that the ultimate matrix of iodine is seaweed, and that it has been and is being produced by the power of vegetable life in seaweed: four molecules of $NaCl$ being converted into $(Na_4Cl)Cl_4 = ICl_4$, a well-known compound.

(*b* and *c*) The heptadic valency is explained by the four valences from Na_4 being quiescent.

Mercury (199) = Na_4Ag .

(*a*) Ag is always found with Hg.

(*b*) The valency is explained by two of the valences from Na_4 being quiescent, the other two being unable to act at the same time as the single one from Ag, so that the element is either dyadic or monadic.

(*c*) Hg cannot act as a non-metal as there is no free $H-H_2$.

Rubidium (85) = Na_4K .

(*a*) Rb is found with Na and K in rhodizite.

(*b*) It acts both as a monad and a triad, so that the two valences from Na_4 are sometimes quiescent and sometimes not.

(*c*) It cannot act as a non-metal, as there is no free $H-H_2$.

Selenium (78) = Na_4S .

(*a*) Se is always found with S.

(*b* and *c*) Its similarity to S is explained by the two valences from Na_4 being quiescent.

Tin (118) = $ZrSi$.

(*a*) Cassiterite (SnO_2) is found in parallel position with zircon ($ZrSiO_4$).

Since, by the Interrelationship of the Elements, $ZrSi = CuAlSi = CuMn$; Sn might also have been formed by the union of Cu and Mn. The alloy $CuMn$ is very like tin.

(*b* and *c*) If the two non-metallic valences of Zr are quiescent with the two metallic valences of Si, the valency of Sn, dibasic and diacidic is explained.

Radium (226) = $ZrBa$.

(*a*) The raw material from which Ra is prepared consists principally of Ba, Sr, and Ca. Ra is also found in pitchblende, which contains zirconium.

(*b* and *c*) If the two valences of Ba are quiescent with the two metallic valences of Zr, there would be left only the two electro-positive valences emanating from the portion $H-H_2$ of Zr. Ra cannot act as a non-metal because there is no electro-negative valence left to unite with a base.

Niton (222) = $Na_4Xe = Ra$ minus $H-H_2$.

(*a*) Nt is found with Ra.

(*b* and *c*) The fact that Nt has no valency is explained by radium's loss of two electro-positive valences when helium is given off; and also by the relation Na_4Xe .

Cobalt (59) = AlS .

(*a*) Cobalt is especially associated with Al-minerals, and is also found with sulphur.

(*b* and *c*) In luteo-cobalt hexachloride = $Co_2(NH_3)_{12}Cl_6$, cobalt has nine valencies, of which Al supplies three and S supplies six. The position of Co in the Periodical Table next to Mn^{VIII} and Fe^{VIII} indicates that nine valences may be expected from it. 59 is almost the only number which could represent an element of nonadic valency according to the theory.

Nickel (59) = SiP .

(*a*) Ni is found in schreibersite (Ni_3Fe_3P) in meteorites. Polydymite (Ni_4S_2) is found with quartz (SiO_2).

(*b*) Ni forms similar compounds to Co, indicating that it also has nine valences, four from Si and five from P.

Molybdenum (96) = Na_4Al .

(*a*) Molybdenite (MoS_2) occurs with cryolite (Na_3AlF_6) in Greenland.

(*b* and *c*) The valency of Mo is exactly explained by the constitution Na_4Al .

Tellurium (128) = MoS .

(*a*) Te is especially associated with Au, Pb, Ag, Bi, Hg; i.e., in the Ag-minerals. Mo is said to be always found with Ag. S is always associated with Te.

(*b* and *c*) Te, Mo and S are all hexads so that the valency is easily explained.

Germanium (72) = As minus H_2 .

(*a*) GeS_2 is found with Ag_2S ($=As_2S_2$) in argyrodite, which occurs in association with minerals containing much arsenic.

(*b*) If the pentad As could give off H_2 with one valence, there would be left an element of atomic weight 72 with four valences.

(*c*) There would be no free $H-H_2$ left, and therefore Ge would not be capable of acting as a non-metal.

Bromine (79) = $AsHe$.

(*a*) Br is chiefly found in combination with Ag, and therefore in ores containing much arsenic.

(*b*) If the pentad As combined with the dyad He, a heptad would be the result.

(*c*) The addition of a free portion $H-H_2$ would make Br non-metallic to a greater degree than As.

The probability that the state of affairs here given with regard to any one of the foregoing 26 elements is the result of accident is 1:3 at least; for in nearly every case the combination of elements given is especially suitable in particular ways which cannot be brought into a probability calculation; and the particular integer is frequently the only one in the neighbourhood, considering six or more adjacent ones, which is at all suitable for explaining the scientific facts concerning the element. E.g., the fact that Ga cannot act as a non-metal has not been brought into the probability calculation, as given below, neither has the fact that none of the ten integers adjacent to 69 could represent a triadic element in accordance with the theory.

There is only one case out of the 26 given, in which an integer in the neighbourhood would be more suitable than the integer found; but this case only helps to emphasise the extraordinary

nature of all the other integers obtained. If Br had been represented by 81 (Na_2Cl) instead of 79 , it would have been a true arithmetical mean between Cl (35) and I (Na_4Cl).

Of the 46 elements from Fe upwards (not including the twelve rare ones) Kr and Xe cannot be considered in any way mineralogically; so that only 44 can come into the following calculation.

The probability that in each of 26 elements the particular number (obtained independently and not arbitrarily by means of the five proofs mentioned in the last paper) would be exactly equal to the sum of the atomic weights of intimately associated elements and at the same time exactly explain the valency, and that neither of the two adjacent integers would be at all suitable for this purpose, is $1 : 3^{44-18 \times 2} = 1 : 3^{17}$ at least; or, considering Ge and Br as exceptions, the probability is $1 : 3^{44-20 \times 2} = 1 : 3^{14}$ at least = $1 : 4$ million.

The remaining 18 elements will be considered in the next two papers, and although they have had to be considered as exceptions to the above reasoning, the facts concerning them will strengthen rather than weaken the conclusions arrived at in this paper.

As an example of the way in which the above reasoning might have been upset, suppose that the two elements which are especially associated with Ag had been As and P instead of As and S, then it would have been impossible to explain how the union of two pentads could produce a monad, knowing that the valences are quiescent in pairs. If it were merely a matter of chance, this sort of thing would be as likely to happen as not; but it never seems to happen except in one or two cases which are only apparent and not real. E.g., the hexad titanium is found with Cb, which is apparently a pentad. But since it is impossible to completely separate these two elements, they must be exactly similar chemically, and therefore, Cb is probably a hexad, the explanation being similar to that given for hexadic Mn (CHEMICAL NEWS, June 4, 1920).

THE MELTING POINTS AND THERMO-ELECTRIC BEHAVIOUR OF LEAD ISOTOPES.

By THEODORE W. RICHARDS and NORRIS F. HALL.

AMONG the properties of the isotopes of lead, the melting points stand out as of especial interest. Since the molecular volumes of these substances are essentially equal (see T. W. Richards and Charles Wadsworth, 3rd, *Journ. American Chem. Society*, 1916, xxxviii., 221, 1658), the question as to whether or not the melting points are likewise equal, compels attention.

Thermocouples were used for this measurement, not only because they could be used with small amounts of material, but also because they are essentially suited to "differential" estimation. W. P. White's papers on this topic afforded many useful suggestions (W. P. White, *ibid.*, 1914, xxxvi., 1856-1885, 2011-2020).

The thermo elements employed were four in number, three single elements and one of four junctions. The difficulty with work at high temperatures is the breaking down or the increasing

conductivity of most insulating materials even below the melting point of lead. Through the kindness of Professor Harvey N. Davis and Dr. F. Wheeler Loomis, asbestos-insulated copper and nickel wire were available for the construction of the elements. This combination has thermoelectric advantages. The thermoelectric effect (about 23 microvolts per degree at 327°) is much higher than that of noble-metal elements, although not so high as copper-constantan; moreover, both sorts of wire are generally very free from the inhomogeneity often met with in alloys, and both metals are sufficiently resistant to oxidation under ordinary conditions.

The use of copper here as well as for connections to the rest of the measuring apparatus diminishes the danger of parasitic effects to a minimum.

The asbestos insulation, which had an inflammable binder, was removed from a few millimetres at the ends of the wires, and the ends were twisted together. They were then soldered with a minimum amount of silver solder, using borax as a flux.

The junctions were insulated from each other by a thin glaze of lead borate prepared from litharge and boric anhydride in a nickel crucible in the proportion represented by $\text{Pb}_2\text{B}_2\text{O}_6$. For convenience in introducing into the glass tube the several separately insulated elements were twisted together and the whole glazed so as to form a single bead. The single element used to measure the bath temperature was simply enclosed in a glass tube. All the "cold ends" were contained in a single glass tube under paraffin. The free ends were, after several windings, soldered firmly to thin copper strips which made contacts through strong clamps (W. P. White, *loc. cit.*, p. 1861).

The furnace consisted of two tall glass beakers, of which the smaller was wound with a commercial resistance wire wrapped in asbestos and placed in the larger beaker. The beakers thus nested were set in the centre of a fibre pile, of which the bottom had been covered with magnesia and asbestos, the whole being packed in this mixture. Around the top of the beakers a smooth covering was made of plaster of Paris. The heavy tempering oil placed in the inner beaker and used for the bath needed renewal from time to time; it carbonised and evaporated but never burned, and its odour, while unpleasant, was not unbearable. The viscous oil was rapidly stirred with a brass stirrer, and the bath was covered with a block of asbestos nearly 3 cm. thick. After the stirrer, the melting point apparatus, the thermo-couples, and a mercury thermometer had all been inserted through the cover, all the holes were luted with a paste made of magnesia, asbestos threads, and oil. The whole furnace was thickly surrounded and covered with wool felt. The rapidity of stirring was such that no difficulty whatever was found in keeping the temperature of the two samples of lead the same within 0.1° while the furnace was rising in temperature at the rate of 10° per minute, or in keeping the furnace temperature constant within 0.05° for hours at a time with proper regulation of heating current. The alternating 110-volt lighting circuit was used as a source of heat, but on account of fluctuating voltage needed frequent regulation if constant temperature was

desired. The heat insulation was satisfactory; cooling curves could be taken with the heating current broken completely. Nevertheless, in order that greater accuracy might be obtained, a small current was usually passed through the heating coil to delay the cooling.

The Electrical Measuring System and Connections.

A 20,000 ohms resistance Wolff potentiometer was employed, instead of an apparatus of lower resistance, because it was somewhat more convenient (especially in that it simplified the standard cell connections) and because even with it, the galvanometer gave all the sensitiveness desirable. The floated battery arrangement described by White (W. P. White, "Constant Battery," *Phys. Rev.*, 1906, xxiii., 447) was used to keep the battery voltage constant, and with about 19,800 ohms in series in the two cells, gave variations so small that it was seldom necessary to change the resistance by as much as 0.1 ohm, in making a balance against the standard of which the voltage was assumed to be 1.0183 ± 0.00004 ($t^\circ = 20^\circ$). Three single-knife switches connected the three single elements with the potentiometer galvanometer circuit, which was provided with an eliminating switch, and a switch for making direct connection with the standard cell. The whole battery circuit was shielded and the shield carried into the eliminating switch. Another switch made connection with the differential element, and at the same time cut out the potentiometer. A suitable protective resistance for the galvanometer was an integral part of the potentiometer.

The galvanometer was a Leeds and Northrup wall type with a mirror. The lamp signal, focused sharply on a translucent scale, was easily read to tenths of a millimetre. The deflection was nearly two mm. per microvolt, so that it was easy to read hundredths of a degree with the single element and thousandths of a degree with the multiple element. All the measuring apparatus was on a single shielded table, under which, but separate from it was a box with the switches of the lighting and heating circuits and the slide resistors for the latter.

The entire measuring system was shielded by a complete equipotential shield, as advocated by White. After the hope that the insulation of oil and glass would prevent leakage from the heating current had proved illusory, the shield was extended into the furnace itself by the device of silver-plating the several parts of the entire melting apparatus, winding their tops with tin-foil and then continuing the winding with thin copper foil. This was wound spirally around the sheaf of connecting wires, forming a continuous flexible protective sheath, and connected into the shield, which quite eliminated trouble from electrical leakage unless the heating current switches were handled simultaneously with some part of the measuring system.

Parasitics were detected and allowed for by means of a suitable eliminating switch. Early in the day's work they were large and often quite variable, but always seemed to become fairly constant and of rather small value about noon when the room and furnace temperatures had reached approximate equilibrium. In the final measurements, they were always tested immediately before

and after the experimental crisis and all trials in which they varied enough to cause appreciable error were rejected.

The two sorts of lead were contained in identical sealed cylinders of Pyrex glass from which the air was exhausted before melting the lead. Each vessel was provided with a smaller co-axial cylindrical glass sheath for the thermo-elements, which thus extended into the centre of the cylindrical mass of lead.

The two kinds of lead were prepared as follows.

Ordinary lead, in the form of acetate, was dissolved, filtered, and precipitated as nitrate from concentrated solution, and then recrystallised (with centrifuging) six times as nitrate from concentrated solution. The purified crystals were then dissolved in warm water in a quartz dish, about 10 per cent of pure nitric acid was added, and the lead was precipitated electrolytically as dioxide in order to eliminate possible traces of silver. The lead dioxide was washed repeatedly, dried on the steam bath, and heated to redness in order to reduce it, at least partially, to litharge and expel any included nitrogen compounds. The orange-red mixture of oxides was then cautiously heated in an unglazed porcelain crucible with potassium cyanide of high purity, until it was reduced to metallic lead, which was next melted in small "alundum" crucibles and poured into a carefully cleaned steel die kindly loaned by Professor P. W. Bridgman. This die, containing the lead, was heated to about 250° , the melting point of soft solder, in a blast flame, and then transferred to a press, where the lead was extruded in the form of wire about 1 mm. in diameter, of which the first three meters were rejected. The remainder of the wire, cut into pieces about 5 mm. long with a clean knife on a glass plate, was introduced into one of the cylindrical lead containers.

The other specimen of lead—the Australian radio-active sample—was treated in the same way, except that the raw material was not the acetate, but rather in metallic form. This was dissolved in nitric acid, evaporated to dryness, taken up with water, filtered, evaporated, recrystallised six times, electrolysed, and after ignition reduced by cyanide as described above.

Samples of each kind of lead were tested spectrographically before and after extrusion through the die, through the kindness of Professor G. P. Baxter. All the samples showed a trace of silver, and the extruded ordinary lead a very small trace of copper. This sample also showed an intensification of one of the lines which appeared in all the lead samples ($\lambda = 3048$); but such intensification is usually not significant, depending rather upon the vagaries of the arc-spark, than upon differences of material. Evidently neither of the samples was perfectly pure—evidently, too, the ordinary lead was somewhat less pure than the other. The maximum impurity probably amounted to not more than five parts in one hundred thousand.

Measurements.

After preliminary trials the method of measurement adopted was as follows. The temperature of the bath was raised rapidly until (with the potentiometer set at the value corresponding approximately to the melting point) the spot of light from the galvanometer was at the extreme low-temperature side of the indicator scale.

Resistance was now thrown into the heating circuit until the passage of the spot of light toward the centre of the scale was sufficiently slow. Readings of E.M.F. were taken every 15 seconds through the melting interval, the heating being so regulated as to maintain a constant temperature gradient between the bath and the charge to be measured. The cooling curve was taken similarly. Marked super-cooling from one to two degrees was the rule, but after this marked depression the temperature rose again to a constant level, which was maintained for a long time. This maximum temperature was taken as the freezing point. The battery voltage was balanced against the standard cell before and after every trial with satisfactory outcome. Corrections for parasitics and galvanometer drift (if any) were made in the immediate neighbourhood of the critical portion of the melting and freezing interval. The super-cooling was greater in the radioactive lead than in the ordinary lead, probably because of the slightly less purity of the latter.

In the first experiments using single elements, the difference between the melting points of the two isotopes did not greatly exceed the probable error of the experiment. In the more sensitive subsequent "differential" experiments, the temperatures of the samples travelled nearly together, differing only $\pm 0.05^\circ$ during wide variations of the furnace temperature above and below the melting point; but they did not remain together in the immediate neighbourhood of the melting point. On heating, a difference in temperature became manifest about 0.5° below the true melting point in the sense that the temperature of the radio-active sample rose more rapidly. Evidently the ordinary lead began to melt at a lower temperature. After reaching the melting point, the difference diminished to less than 0.1° , and afterwards diminished only very slowly until one of the samples melted.

On cooling, as already stated, the ordinary lead crystallised first; but after the radioactive isotope had crystallised, its maximum rose about 0.05° above that of the other. During most of the cooling the radioactive sample showed a temperature about 0.05° above the other. When the heating or cooling was properly regulated and extremely slow it was possible to extend greatly the interval of constancy and to diminish the small unavoidable constant error which tended to increase the apparent difference due to the fact that the ordinary lead was always in a more advanced state either of melting or of freezing than the radioactive.

There seems to be no question then that the radioactive lead showed the higher melting point by about 0.05° or 0.06° —a difference of only one ten-thousandth of the absolute melting temperature of lead. Part of the difference is unquestionably due to slight impurity in the ordinary lead, as shown by the spectroscopic and also by a slight obliquity of the melting curve even under the best conditions of heat supply. Possibly all of the difference may be due to this cause. Certainly there is no difference between the melting points at all comparable with the difference between the atomic weights, which was almost 0.5 per cent.

The Australian radioactive specimen used in this test had an atomic weight of about 206.4, whereas pure uranium lead probably

has an atomic weight very near 206. Accordingly the Australian specimen may be supposed to consist of a solid solution of uranium lead and one or more isotopes of higher atomic weight. Ordinary lead being the most probable admixture, we may assume the specimen to consist of about one part of common lead to three parts of the isotope believed to owe its origin to uranium. But ordinary lead also is probably an isotopic mixture. That two chance mixtures of isotopes in different proportions should assume essentially the same melting point is extremely unlikely, if their melting points were different, or if the addition of one isotope caused any appreciable effect on the melting point of another. Hence from the results just recounted, it is fairly safe to conclude that isotopes must be wholly soluble in one another, in perfectly consolute solid solution, and that all have the same melting point, as indeed one would expect. Separation by freezing is obviously impossible.

Time was lacking for the preparation of yet purer specimens, which would have given a more conclusive verdict.

The Thermoelectric Behaviour of Isotopes.

The apparatus being at hand, a test of the thermoelectric behaviour of the two isotopic forms of lead was worth while. Two precisely similar wires of ordinary lead were connected with the galvanometer terminals, and the other ends were joined by wire made of the radioactive lead—one junction being introduced into an ice bath and the other heated gradually to melting in a flame. No deflection in the galvanometer was observed in any of several repetitions of this test, although one ten-millionth of a volt could have been detected. Evidently, then, there is no difference in thermoelectric power between these two kinds of lead. Presumably this behaviour is characteristic of the behaviour of isotopes in general.

It was intended also to compare their electrical conductivity, but the time needed to prepare the wires with sufficient care as to exact constancy of cross section was lacking. Later this test was accomplished by Professor P. W. Bridgman upon the same samples with more carefully drawn wire. He has described these experiments in another place (Bridgman, *Proc. Nat. Acad. Sci.*, 1919, v., 351-3). He found no difference (beyond the range of experimental error) in the conductivity of the two kinds of lead nor in the effect of pressure or temperature upon their conductivity. We are glad to acknowledge our indebtedness to the Carnegie Institution of Washington for much of the apparatus used in this research.

Summary.

In this paper experiments are described which show that the difference in the melting points of two specimens of lead differing 0.8 in atomic weight is, if appreciable, not over 0.05° . From this outcome, it is fairly safe to assume that the kinds of lead not only have very nearly the same melting point, but also (since the sample consisting chiefly of the lighter isotope doubtless contained ordinary lead) they mix (or rather mutually dissolve) without affecting the melting point.

The Seebeck thermoelectric effect produced at a junction of the two kinds of lead is also shown to be nil.—*Journal American Chemical Society*, August, 1920.

ADDRESS TO THE ENGINEERING SECTION OF THE BRITISH ASSOCIATION.

By Professor C. F. JENKIN, C.B.E., M.A.,
President of the Section.

(Concluded from p. 173).

IF we admit that the fatigue limit is the proper basis for engine-strength calculations, there are a number of interesting modifications required in the common theory of the strength of materials. It will no longer be possible to neglect, as has been so general in the past, the uneven distribution of stress in irregularly shaped parts of machines. It has been generally recognised that sharp corners should be avoided when possible, but no theory is available to enable the stresses at corners to be calculated or to enable their effect on the strength of the member to be estimated. If fatigue is the critical factor in failure under fluctuating stresses such theory is most necessary. Even the roughest guide would be of great value. The nature and magnitude of the concentrations of stress which occur in practice have been investigated experimentally by Professor Coker by his elegant optical method which has given most valuable results, some of which are already being used in designing offices. If the mathematical theory is too difficult, it may be possible to lay down practical rules deduced from such experimental results—but the method still has many limitations, perhaps the most serious being that it can only be used on flat models. I believe Professor Coker expects to be able to extend the method to round models.

As a simple example to show the importance of the subject let us consider the effect of a groove round a straight round bar subject to alternating tension and compression—such a groove as a screw thread. There will be a concentration of stress at the bottom of the groove. The ratio of the stress at the bottom of a groove to the mean stress in the bar has been worked out mathematically by Mr. A. A. Griffith, and his calculations have been confirmed experimentally by his elegant soap-bubble method. The ratio depends on the relation between the depth of the groove, the radius at the bottom, and slightly on the angle between the sides. For a Whitworth form of thread the ratio will be about 3. If the Fatigue Limit is exceeded at the bottom of the groove the metal will fail and a minute crack will form there; this crack will soon spread right across the bar and total failure will result. Thus we see that the safe mean stress in the bar will be reduced to one-third what a plain bar will bear. The truth of this theory regarding the importance of concentrations of stress has still to be proved experimentally; if true, it is of far-reaching importance, since it applies to all concentrations of stress in machine parts subject to fluctuating loads.

The theory does not apply to steadily loaded members; in these the local excess of stress is relieved by the stretching of the minute portion which is overloaded, and no further consequences follow.

The theory appears to apply to grooves however small, and has an important bearing on the smoothness of the finish of machine parts. The

surface of any engine part finished by filing is certainly entirely covered with scratches. Emery likewise leaves the surface scratched—though the scratches are smaller. If, however, polishing be carried further the surface may ultimately be freed from scratches and left in a burnished condition. In this condition amorphous metal has been smeared over the surface—the smooth appearance is not simply due to the scratches being too small to see. The strength—under alternating stresses—appears to depend on the form of the scratches, and if the ratio of radius at the bottom of the scratch to its depth is fairly large, very little weakening occurs. It seems probable in the ordinary engineering finish produced by emery and oil that the scratches are broad and shallow. This subject is being investigated. A considerable amount of evidence has been collected from practical experience pointing to the important effect which a smooth finish has on the strength of heavily stressed engine parts.

Fatigue is probably the cause of failure of wire in wire ropes. A good deal of valuable experimental work has been done on the life of ropes, but so far as I am aware there is no satisfactory theory of their strength. This subject also requires research, and it seems probable that valuable practical results might follow if the true explanation of the cause of the breakages of the wires was determined.

These are only examples, but they may be sufficient to show how much work, both experimental and theoretical, requires to be done to give the engineer a really sound basis for the simplest strength calculations on any moving machinery. But there are more fundamental questions still which must be tackled before the simplest questions of all which meet the engineer can be answered scientifically. The two most urgent and most important questions which I met with during the war in connection with aircraft were always the same—Why did some part break? and, What is the best material to use for that part? It was most disconcerting to find how inadequate one's knowledge was to answer these two simple questions. The common answers are: To the first—"It broke because it was too weak, make it stronger," and to the second—"General practice indicates such a material as the best—better not try any other or you may have trouble." In aircraft, weight is paramount, and to make a part stronger—i.e., heavier—had to be the last resort, and when used was almost a confession of failure. "General practice" was no guide in aeroplane engines, which are built of the strangest materials. The origins of fractures were traced to many causes, often lying far away from the site of the breakage; but with these I am not concerned today. I wish to confine our consideration to the actual fracture and to ask, "What stress caused the fracture?" and "What property of the metal was absent which would have enabled it to withstand that stress?" And again, "What other material possesses suitable properties to withstand the stresses better?" These are the fundamental questions which I have referred to—and which urgently need answers.

As an example I will take a broken propeller shaft. It has broken in a beautiful spiral fracture. What stress causes that? I have failed to explain it by any of the facts I know about the

steel it is made of. It is, of course, a fatigue fracture—i.e., it spread gradually. The questions to be answered are: "Did it fail under tension, bending or torsion?"; and, "Why was a spiral direction followed by the failure as it spread?"

It may be objected that the question is unimportant. I think not. For example, till we can determine the nature of the stress we cannot indicate the nature of the load—thus I cannot say if it broke under a torsional load (possibly torsional vibration) or under a bending load (possibly due to some periodic variation of thrust on one of the propeller blades as it passed an obstruction). Until the nature of the load which caused the failure is known, it is very difficult to take steps to guard against similar accidents. For the most urgent reasons, therefore, we require to be able to understand the fracture, as in nearly all aircraft problems men's lives hang on the answer.

Turning now to the question of the most suitable material, I will take as an example the material for the crankshaft of an aeroplane engine. A few months before the Armistice there were difficulties in getting sufficient supplies of the high-grade nickel-chrome steel forgings then in general use for shafts, and proposals were made to use a plain carbon steel. Such a steel would be about 30 per cent weaker, according to the ordinary tests. A conference of leading metallurgists and engineers was held to discuss the suggestion. No one present ventured to predict whether the weaker steel would answer or not, or whether the dimensions would have to be increased or not. It was pointed out that a French engine was now using 50-ton steel with better results than when using the 100-ton steel for which it was designed, no changes in dimensions having been made. Such a reduction of strength might be understood in ordinary engineering where there are large margins of safety, but in an aeroplane engine, in which every ounce of metal is cut off which can be spared, they show how completely ignorant engineers are of what the suitability of material depends on.

As another example, Why are oxygen cylinders annealed—repeatedly? Annealing reduces the steel to its weakest condition. I believe the fondness for annealing is due to our ignorance of the properties we require. Perhaps the quality of steel which an engineer fears most is brittleness. He believes that annealing will soften it and reduce the brittleness; so he anneals, blindly. The fact is that we do not know what brittleness is—we cannot define it—we cannot measure it—though there are endless empirical tests to detect it. Till we know what it means and can measure it we are in a miserable position. During the war I was consulted on what could be done to reduce the enormous weight of oxygen cylinders, and I advised that experiments should be made on the high-quality alloyed steel tubes we were using in aircraft construction. The department dealing with these tubes took the matter up, and alloyed steel cylinders, properly heat-treated, were made. These were, I believe, a success, and only weighed a small fraction of the old-fashioned cylinders. But my suggestion was little more than a guess, and no means was known of accurately testing the suitability of the material, so they were only accepted after passing any number of empirical tests, consisting of various kinds of rough usage, to see if they would crack or burst. Surely an

engineer should be able to say whether a cylinder is safe without dropping it from the roof or rolling it down the front-door steps to see if it breaks.

These examples refer only to different grades of the same material—steel—but how far worse off we are when the problem is whether some other alloy would be suitable to replace steel. Proposals have been made, for example, to replace the very hard steel used at present for connecting rods by duralumin or some other forged aluminium alloy. It seems worth trying; but who, in our present state of ignorance of the real properties of metals, will say if the experiment will be a success?

How difficult it is to prophesy may be illustrated by the results of two empirical tests on duralumin and steel sheets of the same thicknesses. The ultimate strengths and elongations of the steel and the duralumin were roughly equal. The lantern slides show that under reverse-bend tests they follow the same law, the steel being the better. But under the cupping test they follow opposite laws.

The suitability of different materials presumably depends on their fundamental physical properties. These may be many, but some physicists think that they are probably really very few, and that, knowing these few, it may be possible to deduce all the complex properties required by the engineer and to state with certainty how materials will behave under any conditions of service. This is the most fundamental problem which needs solution to enable the knowledge of the strength of materials to be put on a sound foundation. It will need the co-operation of able physicists, metallurgists, and engineers to solve it.

While urging the importance of research in the fundamental theories of stress and fundamental properties of materials, I wish to lay special stress on the nature of the researches required. Engineers are intensely practical men, and their practice has generally been ahead of their theory. The difficulties they have met have been dealt with often with the greatest ingenuity and skill, as special problems. They have seldom had time or opportunity to solve the general problems, and as a result they are used to making their experiments and trials as close a copy—usually on a smaller scale—of the real thing as possible. The results obtained in this way, while they are applicable to the particular problem, are of little general use. They depend on many factors. The researches I am now advocating must be of a diametrically opposite description. They must be absolutely general, and the results must depend on one factor only at a time, so that general laws may be established which will be applicable to all special problems.

There are many other similar gaps in our knowledge to which I have not time to refer to to-day. I have tried to show that we need most of all a real knowledge of the fundamental properties of materials, from which we shall be able to deduce their behaviour in any condition of service, so that we may be able to compare the relative merits of diverse materials for any particular purpose.

Secondly, that we need a practical method of calculating the stresses in parts of any form, so that concentrations of stress may be avoided or that their magnitudes may be known and allowed for.

Thirdly, that we need a rational connecting link between the tests made on materials and the stresses they will bear in service, to replace the factor of safety. I have suggested two tests, the Proof Load and the Fatigue Limit, which might be used directly in estimating the allowable working stress.

Fourthly, that we need a mathematical theory for the strength of anisotropic materials, of which timber is an extreme and important example.

When the notes for this address were first drafted, I ended by an appeal to the Board of Scientific and Industrial Research to undertake the necessary research work. Since then the Aeronautical Research Committee has been constituted, and a sub-committee has been appointed to deal with "Materials." I have great hopes that the committee will tackle many of these problems. I will therefore conclude by appealing to all who can help to assist that committee in their endeavour to solve these most important and fascinating, but most difficult, problems.

CANADA AS A SOURCE OF HELIUM.

EARLY in 1915, Dr. J. C. McLennan, professor in charge of the Department of Physics at Toronto University, was requested by the Board of Invention and Research, London, England, to investigate the helium content of the natural gas supplies within the Empire. The necessity for such an investigation and the importance of it was, of course, the replacement of helium gas for hydrogen in aeronautics. The results of this investigation have been offered to the Mines Branch of the Department of Mines of Canada by Dr. McLennan, and now appear in bulletin form, "Bulletin No. 31, Report on Some Sources of Helium in the British Empire." Recently also (June 17) Dr. McLennan before a crowded meeting of the Chemical Society, London England, gave a lecture in which he described the developments which led up to the manufacture of helium on a large scale for war purposes. It has been shown that the largest source of supply of helium at present known within the Empire is located in Canada.

The importance of this work of Dr. McLennan and his associates cannot be over emphasized, not only as a great war work, but also as the commencement of the production of helium on a commercial scale from certain Canadian natural gases. It is interesting to note that Dr. Alfred W. G. Wilson, Engineer in Charge of Investigation of Chemical Industries, states in his letter of transmission of Dr. McLennan's manuscript to Dr. Eugene Haanel, Director Mines Branch, "this production (of helium) may become an important factor in the development of an aeronautical service in this country and probably in other parts of the Empire." From the Mines Branch Report, and from Dr. McLennan's address to the Chemical Society the principal points in connection with the work on helium would seem to be the following: Helium has been found in varying quantities in most of the natural gases of Canada, but the Blackheath field in South-Western Ontario, and the Bow Island Field in Alberta have tested out the largest percentage of helium, in the former 0.34 per cent, and in the latter 0.34 per cent.

In New Brunswick the helium content was only 0.064 per cent, according to a determination made by R. T. Elworthy. In British Columbia the helium content of the natural gas was from 0.003 to 0.028 per cent.

The principle gases found in natural gas are methane, ethane, nitrogen, oxygen, helium, and carbon dioxide.

Production of Helium.

In the spring of 1916, Dr. McLennan made a report in which he recommended that a semi-commercial unit should be erected and a trial made to see whether the helium could be extracted from the natural gas. The Admiralty authorities at first did not favour the idea, and it was not until the middle of the summer of 1917 that the Admiralty authorities concurred in this plan, and commissioned him to proceed with the actual production of helium. As there were large quantities of natural gas in Texas, Dr. McLennan suggested that the American Government should develop that field. The Americans had already commenced work there through a communication from the late Sir William Ramsay. The American Army and Navy however were not very appreciative of the value of such work in Texas, though their Bureau of Mines was interested. In August, 1917, Dr. McLennan and his associates made an actual start at production at Hamilton, Ontario, after very considerable difficulty in securing the proper apparatus, borrowing a Claude oxygen-producing column from the works of the company working that process in Toronto, getting a compressor at Oldbury, England, through the kindness of Sir George Beilby, and some cylinders from the Royal Air Force. In this way he got some cylinders and two or three pumps which were sent over to Canada, and by March, 1918, he had produced at Hamilton a large quantity of helium of 87 per cent purity. The American Government had in the meantime, as a consequence of what was being done at Hamilton, set aside one-and-a-half million dollars, which was divided between their Mines Bureau, the Linde Company, and the Air Reduction Company, and commenced work on production in Texas. Later on, the Americans produced large quantities, and by the time of the Armistice, had produced about 160,000 cubic feet. Their method was different from that used by Dr. McLennan at Hamilton, and proved very expensive. They had a closed cycle for the carbon-dioxide, and a closed nitrogen cycle. The United States Bureau of Mines, not satisfied with the results, had experimented with a Norton Jeffries machine, originally designed to produce oxygen, and Dr. McLennan stated in his London address that he believed they were still working at this machine, as he had received no intelligence that they had been able to produce helium with it as yet.

Dr. McLennan does not believe that there should be any particular difficulty in developing suitable apparatus for securing helium from natural gas. The main point to consider and the chief difficulty was to secure proper balance between heat exchangers, liquefiers, vapourising columns and rectifying columns, so that each gas could be liquified out at its suitable temperature, and by the exchange of cold or heat, carry out the operation in the most economic possible way. Having settled finally which column would do the

work, after a series of trials, a station was established at Calgary, Alta., in September, 1918. The final type of column, however, was not evolved from the original Claude column until the summer of 1919, and with this machine helium was regularly produced of a purity of 87.90 per cent. The latest type of machine had been in use from December 3, 1919, until April 17, 1920, and in that time the rate of production had doubled. In April, the plant was producing 700 to 800 cubic feet per run. In one week it produced nearly 2000 cubic feet. With further experience, Dr. McLennan believes that it would be possible to obtain helium gas of 97 per cent purity, and with an efficiency of 80 per cent. The estimated cost of production is less than 2½d. per cubic foot. The market price for the gas in 1914, if it were possible to secure any, was £300 per cubic foot.

At the close of his lecture to the Chemical Society, Dr. McLennan pleaded strongly for the establishment of a cryogenic laboratory, in order that a laboratory and supply station might be maintained, preferably at Calgary. The capital sum required would be £35,000, while the interest on £125,000 or £150,000 would maintain the station.

It is announced that the Honorary Advisory Council of Scientific and Industrial Research of Canada has awarded the sum of \$5000 to assist Dr. McLennan in his work on conserving helium.

It is well to remember that Canada is the only part of the Empire that contains helium in any worth-while quantity. The helium content of the gas in New Zealand is only 0.77 per cent, while gases tested in Italy contained no helium whatever. In his work on helium investigations, Dr. McLennan received valuable assistance from his colleagues, Professors John Satterly, E. F. Burton, and H. F. Dawes, of Toronto University; Captain H. A. McTaggart; Mr. John Patterson, of the Meteorological Branch, Ottawa; and Messrs. V. F. Murray, E. Edwards, J. T. F. Young, H. J. C. Ireton, and Mr. K. H. Kingdon, of Toronto University. — *Canadian Chemical Journal*, September, 1920.

NOTES.

UNIVERSITY OF BIRMINGHAM.—The Council and Senate of the University of Birmingham launched an appeal this week for half-a-million pounds. The University is growing at an enormous rate, and extension is necessary, if the students are to be retained. The growth in their number has been phenomenal, particularly in applied science, and all the industrial and technical faculties are crowded out. Sir Gilbert Barling, the Vice-Chancellor, told a CHEMICAL NEWS representative that it seemed a paradox, but it was true, that the greater the extent of the strength of the University with respect of students the greater the loss in money. This was explained by the fact that the students fees only covered a little more than the actual cost, and the Senate did not desire further to increase fees because that might drive away the very kind of student they wished to encourage. "We want it to be a democratic University," said the Vice-Chancellor, "and we want manufacturers to help us, because the

amount of financial help we get from the Government will be largely determined by the sum we can raise." The Faculties of Physics and Chemistry have been removed with others from Mason's Science College to the Barnbrook Buildings, and ten army huts 70ft. by 30ft. have been erected as temporary laboratories, &c.

THE SOCIETY OF DYERS AND COLOURISTS.—The Council announces that the Rt. Hon. Lord Moulton, P.C., K.C.B., G.B.E., F.R.S., will give his Presidential Address in the Council Chamber, Town Hall, Bradford, on October 15, at 3 p.m.

MEETINGS FOR THE WEEK.

Tuesday, October 19.

Institution of Petroleum Technologists, 5.30. "Coal as a Source of Oil Fuel Supply," by Sir Arthur Duckham.

Wednesday October 20.

Royal Microscopical Society, 8.

Thursday, October 21.

Institution of Mining and Metallurgy, 5.30.

Friday October 22.

Institution of Mechanical Engineers, 6. Presidential Address.

NOTICES.

EDITORIAL.—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the Editor.

SUBSCRIPTIONS, £1 18s. per annum, payable in advance, should be addressed to the MANAGER.

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T. J. REES, B.A.,
Director of Education,
Education Offices,
Swansea.

11th October, 1920.

LEEDS UNIVERSITY.

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THE Council will shortly proceed to the appointment of a Lecturer and Research Chemist in Colour Chemistry and Dyeing, at a salary of £450 a year. Preference will be given to a candidate with some works experience. Applications should be sent to THE SECRETARY, The University, Leeds, from whom further particulars may be obtained.

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R. M. WILSON, Principal.

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CHELMSFORD.

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R. M. WILSON, Principal.

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COLEG PRIFATHROFAOL
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Further particulars may be obtained from the undersigned, by whom applications with testimonials (which need not be printed) must be received on or before Saturday, October 23rd, 1920.

October 11, 1920. D. J. A. BROWN, Registrar.

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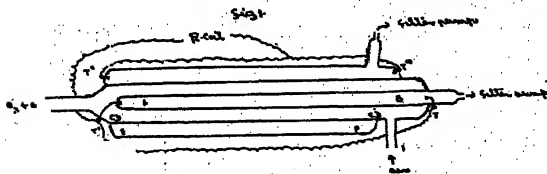
A NEW FORM OF OZONISER FOR LABORATORY WORK.

By Y. V. RAMAIAH and M. V. N. SWAMY, B.A.

General.

THE importance of ozone as a means of research in a laboratory is growing day by day. It almost became an indispensable reagent in organic chemistry in matters of determining the chemical constitution of unsaturated compounds. As the demand for ozone is immense and the ozonisers that are used in the laboratory are inefficient to meet the demand, the authors wish to bring before the scientific world a new form of ozoniser which is simple and certain. Dealing with the production of ozonised air or oxygen, the authors do not propose to draw invidious comparisons between the few ozonisers that are known to the scientists; suffice it to say that there is not a single ozoniser simple and easy of construction, effective as an ozone producer, whether from oxygen or air, easily and quickly repaired. So in pursuing this inquiry, the following considerations were kept prominently in view in the construction of the ozoniser:—

1. Simplicity of design.
2. Capacity to produce pure ozone.
3. To ozonise to a maximum a current of air or oxygen.



The first consideration is attended to in the construction of the ozoniser by making use of the most ordinary appliances at present found in any laboratory. As to the second point, the tendency to sparking is completely avoided and as such no chance is given to the production of nitrogen oxides in the corona. The last aim is secured by using a large ozonising surface and by even distribution of potential along the faces of the dielectrics which is done by using a rarefied gas as a conductor of electricity. Another feature of this new departure is that it renders the instrument to work under all conditions and makes it easy of manipulation.

The description of the Instrument.

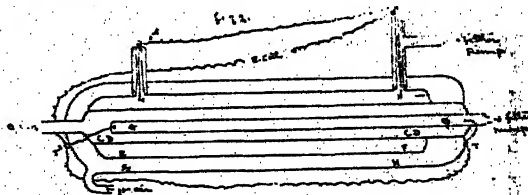
The diagrams are self-explanatory, and as such no elaborate descriptions of the instruments are needed. AB, CD, and EF are three concentric glass tubes, fused into one another as shown in the Figures. When fusing becomes a difficult job, all the joints can be made of sealing wax and paraffine. The chambers AB and EF are exhausted by means of filter-pumps. The diminution of the pressure which a good filter-pump can secure is sufficient to make the gas conduct the high tension electric current. T, T', T'', and T''' are platinum terminals ending in small discs fused into the glass tubes AB and EF. The elec-

trodes are made as short as possible within the tubes. I is the inlet tube for air or oxygen, and O the outlet tube for ozone. In the second apparatus the outermost tube is made of aluminium. In this case the electrodes are led into the tube EF through thick glass tubes as shown in Fig. 2. The advantages that accrue by using an outer case as aluminium are:—

1. The gas can be conveniently cooled.
2. The gas is exposed to the silent electric discharge twice before it comes off finally, once in the annular space between the aluminium tube and the tube EF, and again in the annular space between the tubes AB and EF. This treatment of the gas surely results in an increased production of ozone.

The Method of Estimation of Ozone.

The most commonly used method of estimating ozone by potassium iodide is abandoned by us for certain obvious reasons that it gives inaccurate results. The results of estimating ozone by sodium sulphite or sodium arsenite solution vary considerably, and cannot be taken even as approximately accurate results. So, the method suggested by E. Molinari and Socini (*Ber.*, 1906, xxxix., 2735-44) is worked out by us. P. Fenaroli had previously worked at the method and found that it gave very good results (*Gas. Chin. Ital.*, 1906, xxxvi., 292-298). Molinari and Socini have found that unsaturated fatty acids take up quantitatively ozone. Where the introduction of ozone produced thickening of the oil it is necessary to use a solvent, but oleic acid takes up ozone without the use of any solvent.



One molecule of oleic acid takes up one molecule of ozone. The oil is contained in a five-bulb apparatus as used in combustion work, and the gas containing ozone is passed through the oil at the rate of 150 bubbles per minute; the temperature is maintained below 40° and above 10°. A calcium chloride tube is joined on to the absorption bulbs, as it was found that even a carefully dried oil gives off a little moisture during the experiment. The increase in the weight of the oil corresponds exactly to the addition of a molecule of ozone for each double linking of the fatty compound.

Results.

The diameter of the tube AB is 30 mm., that of CD 34 mm., and that of EF 70 mm. The length of the apparatus is 800 mm. The annular space between the aluminium tube and the tube EF is 1.5 mm. With the first apparatus, a yield of 40-50 mgrms. of ozone per litre of oxygen is obtained, and with the second apparatus a yield of 50-60 mgrms. of ozone per litre of oxygen. Both the instruments are worked at 15° C., and the oxygen used is dried by phosphorus pentoxide. The length of the spark of the induction coil is about 2 inches.

Maharajah's College, Vizianageram, S. India
2nd March, 1920.

TABLE I.—*World's Production of Borate Minerals.*

	1913	1914	1915	1916	1917	1918
Italy (crude boric acid)	2,410	2,537	2,497	2,293	2,335	2,210
Argentine Republic (calc. borate) ...	933	613	192	86	—	—
Chile (calcium borate)	50,225	31,907	14,869	12,565	—	—
Peru (borates)	2,001	1,263	510	1,289	800	523
United States (crude borates) ...	52,678	56,624	60,801	93,943	98,798	80,575

DETERMINATION OF ZIRCONIUM IN
ZIRCONIA ORE.

1.2408 grms. of zirconia ore was fused with 12 to 15 grms. of potassium hydrogen fluoride in a platinum dish. The potassium hydrogen fluoride was prepared by treating potassium fluoride with a slight excess of hydrofluoric acid and evaporating over a very small flame until a clear fused mass was obtained. After allowing it to cool, it was broken up. The mixture of zirconia ore and fluoride was carefully heated by a very small flame. When the mixture became fused, it was stirred with a platinum rod, and the size of the flame was gradually increased. After the whole had become solid and white, it was heated over a powerful burner until it just fused to a clear liquid. The lowest possible temperature for this operation was always used. The cooled melt was next treated with about 50 cc. of 1:1 sulphuric acid, gently heated until nearly all water was removed, and then more strongly heated until abundant fumes were evolved. The cold residue was boiled with water, cooled, and diluted to 250 cc. 100 cc. of this solution was diluted, boiled, and precipitated by ammonium hydroxide in the presence of ammonium chloride. The hydroxides were filtered off and well washed. The filter paper and the precipitate were treated with 36 cc. of conc. hydrochloric acid and about 40 cc of water, boiled, diluted to 700 cc., and precipitated by selenious acid. (If phosphoric acid is present, the insoluble phosphate must be filtered off and treated as mentioned under phosphoric acid). The insoluble selenite was removed by filtration, washed with 3 per cent hydrochloric acid, dried and ignited. The resulting oxides weighed 0.4286 grms. 50 cc. of the solution treated in a similar manner gave 0.2141 grms. These quantities represented 86.36 and 86.40 per cent respectively, of zirconium and titanium oxides.

Average by selenious acid ... 86.38 per cent.

By cupferron was ... 86.36 per cent.

0.2591 grms. of another sample of zirconia ore gave 0.1939 grms. of oxides of zirconium and titanium, or 74.84 per cent, while the average given by cupferron was 74.70 per cent.

The method described above was found to be very rapid, simple, and accurate for the determination of zirconium. The reagent, selenious acid, is cheap.

The determination of thorium by means of selenious acid and the determination of tantalum and columbium by means of cupferron are being investigated at the present time.—*Journal of the American Chemical Society*, September, 1920

MINERAL RESOURCES OF THE WORLD.

Borates.

THE world's production of borate minerals for the years 1913 to 1919 inclusive, is (according to a pamphlet issued by the Imperial Mineral Resources Bureau, entitled, "The Mineral Industry of the British Empire and Foreign Countries") as shown in Table I.

Natural borates of commercial importance are found as (1) borax (hydrated sodium borate); (2) ulexite (hydrated borate of sodium and calcium); (3) Colemanite (hydrated calcium borate); and (4) boracite (borate and chloride of magnesium).

Table II. shows the composition of these borate minerals.

TABLE II.

	Colemanite (California)	Ulexite (Chile and Peru)	Boracite (Asia Minor)
Boric Acid	40.19	44.38	45.89
Lime	31.89	16.14	30.62
Magnesia	1.50	0.91	0.53
Iron and Alumina	0.62	0.48	0.98
Soda	—	6.50	—
Sodium Chloride	—	7.46	—
Carbon Dioxide	8.53	—	—
Sulphur Trioxide	0.26	3.35	1.25
Water and organic matter	5.83	16.25	17.09
Insoluble matter	11.18	4.71	3.64
	100.00	100.18	100.00

The uses of boron and its compounds are enumerated, and it may be useful to give a resumé of them.

Borax is a valuable flux for chemical and metallurgical purposes. It is used in the manufacture of pottery glazes and enamels, and as a glaze for paper and linen. It is used in tanning and glue manufacture, also in the manufacture of soap and glass. As an antiseptic it is used as medicine and as a food preservative.

Chromium borate is used as a pigment in calico printing.

Borates of manganese and lead are used as drying agents in the paint trade.

The perborates of sodium and calcium are used to generate pure hydrogen peroxide.

Boron is added to metallic castings to strengthen them, especially those of aluminium and nickel.

LIEBIG'S EXTRACT OF MEAT COMPANY, LIMITED.—Mr. J. Percy Clarke, C.B.E., M.Inst.C.E., has been elected to the Board of the Liebig's Extract of Meat Company, Limited, to fill the vacancy occasioned by the death of the late Mr Maurice Glyn.

THE METRIC SYSTEM.

THE Report of the Committee appointed by the Conjoint Board of Scientific Societies to consider the compulsory adoption of the Metric System has been issued. It deals exhaustively with the subject, and after a very impartial discussion makes the following recommendations:—

Weights and Measures.

Your Committee recommends:—

I. That the British system of units of weights and measures be retained in general use in the United Kingdom; that no proposals for modification of these units with the object of improving their inter-relation be entertained; and that no new fundamental unit be established. In preference to any such alteration, the Committee would recommend the whole-hearted adoption of the Metric System.

II. That, while the Committee does not recommend the general adoption of the Metric System for internal use, it nevertheless considers that a definite movement towards compiling statistics in Metric units, or in Metric and British, but not in British alone, should be set on foot. It recommends that, wherever possible, alternative scales of Metric and British units should be shown as on geographical maps, cadastral maps, and plans; that, whenever possible, contours should be shown in metres and not in feet; and that whenever data of any description are published which will be used in conjunction with foreign data, the Metric equivalents should be given if Metric units are not employed alone.

III. That serious attention be given to the decimalisation of British weights and measures, and to the elimination of those which do not lend themselves readily to this purpose; but the Committee insists still more strongly on the primary reform that quantities should be expressed in terms of a single unit, rather than in a complex of units. Thus, while it would not propose the disuse of such units as the mile, the yard, the foot, and the inch, it would insist that distances should be expressed in miles and decimals of a mile, or in feet and decimals of a foot, but not in any complex of miles and yards, feet and inches; that railway charges should be calculated in tons and decimals of a ton, or in pounds, but not in hundredweights, quarters, and pounds; and so on. The Committee believes that if an intelligent lead in this direction were given by the various Departments of State, a great part of the arguments against the British system would be swept away.

On this principle it suggests the following simplifications of the British system:—

Measure of Length.—The abolition of the pole, furlong, and league; the limitation of the link and chain to use in the determination of area.

Measures of Weight.—The abolition of the grain, dram, stone, quarter, and hundredweight of 112 pounds, and the complete abolition of Apothecaries' Weight.

Measures of Capacity.—The use of the gallon as the general standard, with the customary subdivision into quarts and pints for retail use, but not otherwise; the abolition of the peck, bushel, quarter, chaldron, and barrel, and the substitution of measure by weight.

Measures of Areas.—The abolition of the square rod or perch, and the rood, all areas of land being in acres and decimals, or in square feet for small plots, and all other superficial measures being in square feet.

IV. That in the use of the Metric System many of the names of multiples and subdivisions of units should be omitted: otherwise it is to be feared that British habit will tend to say, 4 metres, 7 decimetres, 9 centimetres, 4 millimetres, instead of 4.794 metres or 4794 millimetres. The Committee also recommends that the recent French proposal for rejecting the use of units of capacity as distinct from units of volume should be followed. The Committee calls attention to the very inconvenient names of the proposed new French units, especially of the *sthène*; it would agree to the proposal to call the centigrade scale of temperature the centesimal; but it would resist any proposal for the centesimal division of the quadrant. It is impressed by the need for very careful examination of the abbreviations to be used for the various units, and by the importance of defining the standards in terms of the international prototypes instead of the national copies.

V. That the use of the metric system be made compulsory with as little delay as possible in the whole trade in fine chemicals and drugs, and in all specifications and prescriptions relating to such products.

Coinage.

VI. That no change in the existing system of British coinage be attempted in present circumstances.

Legislation.

VII. Very little legislative action would be required to give effect to the recommendations of your Committee if they were adopted. Having regard to the character of the various proposals for legislation which have been put forward by the Decimal Association and other responsible bodies, the Committee consider that it may be useful to make certain general observations upon the conditions which should, in their judgment, be observed in giving effect to any proposals of this nature.

VIII. The "Metric System" must be sufficiently defined, especially in view of the considerable extension of the system under consideration by the French Government and discussed in Sections 16-26 of this Report. There must be explicit reference to the International Metric Convention. The Board of Trade copies must not be defined as standards without reference to their errors in comparison with the international prototypes. The Parliamentary copies must not be required of iridium-platinum without consideration of substituting nickel-steel or quartz. The respective equivalents between British and metric measures must be defined in the Schedule; this is particularly necessary in view of the difference between the existing legal equivalents in the United States and Britain.

IX. If the metric system of weights and measures be enforced, but the decimal use of numbers not enforced, there would be nothing to prevent the continued dealings in dozens, scores, conventional hundreds of 60 and 120, bakers' dozens, and so on, which form so confusing a feature of the present British practice.

X. In addition to a schedule giving the denomination of the Board of Trade standards, that is to say, the denominations in which weights and measures may be made, there must be a careful statement of authorised terms in the metric system. For example, the kilometre and cubic metre do not appear in a certain schedule because there are no Board of Trade standards of those denominations; whereas dekametre, dekalitre, hectogramme, and dekagramme do appear. There is some danger that such a schedule should be taken as establishing and recommending the use of these names. But if the Metric System is to be adopted in any branch of British practice, your Committee believes that efforts should be made to restrict the number of terms to be employed, and great care should be taken in establishing a sound practice in this matter.

XI. In its opinion, it is also highly inadvisable to use terms such as metric gallon for 5 litres, metric pound for 500 grammes, metric chain for 20 metres, since such attempts to suggest relation between the new system and the old would be more likely to lead to confusion than convenience.

XII. In any legislation there must be careful provision for official supervision of revised railway and other rates, to avoid increases all round against the public; and there must be provision for dealing with standard sizes of printing paper, photographic plates, and a thousand other things usually sold in standards, as well as for the registration of tonnage of ships, new postal rates, building regulations and such like. There must be provision for an expected period of transition, if not a complete exception, in the sale of gas and water by existing meters, unless this can be brought about under an "old contracts" clause; and, generally speaking, there must be exceptions allowed in special industries, such as the textile, where the objections to a purely decimal system are very strong, and in special trades, such as the bullion trade, where there is at present a purely decimal, though not metric, system in operation.

XIII. The above considerations are stated as indicating the complicated questions which arise in legislation on weights and measures, to which it may be useful to call attention here.

XIV. Finally, it may not be unnecessary to point out that the drafting of any legislation on the subject requires high scientific and technical knowledge, and that proposals should be submitted for criticism to such officers as the Director of the National Physical Laboratory, the Deputy Warden of the Standards, the Astronomer Royal, and others.

(Signed) H. WILSON FOX, R. A. HADFIELD,
A. R. HINKS, PHILIP MAGNUS, J. PERRY W.
CAWTHORNE UNWIN, W. W. WATTS.

Sir Joseph Thomson, Monsieur le Duc de Broglie, and Mr. Charles P. Sparks have not signed the Report.

Prof. J. Perry has signed the Report, but would favour the addition of a definite recommendation that the sovereign should be adhered to as standard, and that the proposals agreed upon by the Banking Association, the Chambers of Commerce, and the Decimal Association, should be adopted at as early a date as possible.

DETERMINATION OF MOLYBDENUM.

By J. P. BONARDI and EDWARD P. BARRETT.

Introduction.

THIS report presents the results of an investigation by the Bureau of Mines on methods of determining molybdenum. It points out certain disadvantages in the methods hitherto used when applied to low-grade ores, and describes improved methods of both volumetric and gravimetric analysis, perfected in the bureau's laboratories, that are more rapid and accurate than any previously devised. Also, comparison is made of the two methods, as regards their application and relative advantages.

Scope of Report.

During the recent activity in the molybdenum market the old and well-known methods for the determination of molybdenum in ores were found inadequate. They were satisfactory for small tonnages of high-grade material, but, on account of the advent of flotation methods and the inflation of the market because of the war, the tonnage became so large and the grade of products so low that the percentage of molybdenum needed to be determined to the second decimal place.

The failure of analytical methods of determination to keep pace with the magnitude of operations became evident when a tailing sample, from a flotation experiment, which contained 0.13 per cent molybdenum, was submitted for analysis to a reliable commercial laboratory. The laboratory reported a "trace" of molybdenum. The company that submitted the sample was milling 200 tons of ore a day; therefore, if the value of molybdenum at the mill is placed at 75 cents a pound, the 0.13 per cent in the tailing represents a loss or a gain of about \$400 a day. This incident happened during the war, when the Bureau of Mines was making an effort to stimulate the production of molybdenum and at the same time to reduce losses. The Bureau, therefore, began an investigation to devise a more accurate method for determining molybdenum in low-grade ores.

The results of the first efforts disclosed the fact that the required degree of accuracy was difficult to obtain by the various methods in use. The method used must be rapid as well as accurate, as a company treating a low-grade ore must know the results not later than the day after the samples are taken in order to control closely the mill and the mine.

This report presents data and notes collected in the study of the causes for discrepancies and errors found in many methods when used for the determination of molybdenum in low-grade materials. The gravimetric method described was worked on by E. P. Barrett at the Seattle station of the Bureau of Mines, and the volumetric method by J. P. Bonardi at the Bureau of Mines station at Golden, Colo. The preliminary work was done independently, and when the methods had been somewhat mastered, Mr. Bonardi was detailed to Seattle temporarily and results from both methods were compared. Further new data was collected for both methods, and all necessary factors were determined and definitely established by several series of analyses of low-grade ores.

Acknowledgments.

The writers express their appreciation of the assistance of F. K. Ovitiz, superintendent of the Seattle station, and R. B. Moore, superintendent and S. C. Lind, acting superintendent, of the Golden station of the Bureau of Mines, who made it possible for them to work together in the preparation of this report. Credit is due W. H. Coghill, metallurgist of the Seattle station, for suggesting the importance of the work, which he had occasion to bring out in connection with his study of flotation methods for molybdenite. The authors are also indebted to these gentlemen for advice and suggestions offered in the preparation of the report.

Qualitative Tests.

In the analysis of low-grade molybdenum ores, qualitative tests for molybdenum in residues and products are often necessary.

One of the most highly recommended tests is to fuse some of the pulverised ore with sodium or potassium carbonate to which a small amount of potassium nitrate has been added. The fusion is leached with water, heated, and filtered; the filtrate is acidified with hydrochloric acid and boiled several minutes to expel all carbon dioxide. Some ammonium or potassium thiocyanate and a piece of metallic zinc are added; if molybdenum is present a bright cherry-red colour rapidly develops that will disappear on standing in the presence of zinc, the time the colour remains depending upon the proportion of molybdenum present. If hydrogen peroxide is added to the solution immediately after the cherry-red colour has developed, the colour disappears, but returns as soon as the peroxide has been reduced. When only a small proportion of molybdenum is present, if the solution is shaken with a small volume of ether immediately after the thiocyanate and zinc have been added, any colour in the liquid will be extracted by the ether and intensified as a golden brown in the ether ring that forms at the top of the liquid on standing. This makes visible colour that before may have been imperceptible (Prescott, A. B., and Johnson, O. C., "Qualitative Chemical Analysis," 5th ed., 1903, p. 96).

Should the fusion be imperfect and an extraction of iron be present in the leach from the fused carbonates, a cherry-red colour will immediately develop on the addition of the potassium or ammonium thiocyanate to the solution. On adding zinc, however, the colour due to iron disappears, and, unless a large quantity of iron has been brought into solution, this colour will completely disappear prior to the development of any colour due to molybdenum. If this colour reaction of iron and its disappearance on addition of zinc is borne in mind, the above test for molybdenum is infallible (Horton, F. W., "Molybdenum: its Ores and their Concentration": *Pull.* 111, Bureau of Mines, 1916, p. 40).

A standard test for alkaline solutions of molybdates is the addition of tannic acid (Prescott, A. B., and Johnson, O. C., work cited, 5th ed., 1903, p. 97; Moir, James, "Qualitative Tests for Molybdenum," *Journ. Chem. Met. Min. Soc.*, South Africa, 1916, xvi., 191-2). If molybdenum is present the solution will be coloured deep red to brown.

Another test, which is a modification of that given by Scott (see Scott, W. W., "Standard

Methods of Chemical Analysis," 2nd ed., 1917, 275) is to place a pinch of powdered ore on a porcelain lid; moisten with a few drops of nitric acid so as to make a paste, heat nearly to dryness, then add 0.5 cc. of concentrated sulphuric acid, heat to fumes and let stand. If molybdenum is present, breathing on the ore will produce a blue colour; a drop of alcohol added at this point will hasten the colour reaction. The colour will disappear on heating, but the ore is again permitted to stand for some time, will reappear on cooling. Water will also destroy the colour.

An alkaline solution of a molybdate free from iron, after acidifying with acetic acid, will, on the addition of potassium ferrocyanide or tannic acid, become deep red to brown. Pyrogallol, under similar conditions, will give an orange colour. Molybdenum present as ammonium molybdate in a nitric-acid solution is precipitated by microcosmic salt ($\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$) as yellow ammonium phosphomolybdate. The precipitate is soluble in sodium or ammonium hydroxide.

Review of Quantitative Methods in General Use.

Some of the methods for the determination of molybdenum that are in general use are as follows: (1) Precipitation as the sulphide from acid or alkaline solutions with or without increased pressure; (2) precipitation as mercurous molybdate; (3) precipitation as lead molybdate; (4) titration with lead acetate; (5) titration with potassium permanganate; (6) titration with titanium chloride; (7) the iodometric method; and (8) titration with potassium iodate. These methods are briefly as follows:—

Precipitation as the Sulphide.—The precipitation of molybdenum as the sulphide from acid or alkaline solutions, with or without increased pressure, requires either that the precipitated sulphides be converted to some weighable form such as MoO_3 or MoS_3 , or that the sulphides be dissolved passed through a Jones reductor, and titrated with potassium permanganate. The conversion of MoS_3 to MoO_3 is a long and tedious process. MoO_3 is volatile at a temperature of about 400° to 450° C., and complete conversion to MoO_3 requires long ignition at a temperature of about 350° C. Binder (Binder, O., "Estimation of Molybdenum," *Chem. Ztg.*, Jahrg. 1918, xlii., 225; "Abstract in Chem. Abs.," 1918, xii., 2174) states: Molybdenum precipitated as MoS_3 and ignited to MoO_3 is not completely oxidised unless treated with HNO_3 , evaporated, dissolved in NH_4OH , reprecipitated with HNO_3 , evaporated, and ignited. A correction must be made for any trace of matter which remains insoluble when the ignited residue is dissolved in NH_4OH .

In reducing MoS_3 to MoS_2 in a stream of hydrogen in a Rose crucible, many ignitions and weighings are sometimes necessary to obtain constant weights. These processes require considerable care and practice.

Precipitation as Mercurous Molybdate.—The precipitation as mercurous molybdate requires the same care as the preceding method. In addition, chromium, vanadium, tungsten, and phosphorus interfere with the determination (Scott, W. W., "Standard Methods of Chemical Analysis," 2nd ed., 1917, p. 279).

Precipitation as Lead Molybdate.—Regarding the precipitation as lead molybdate, Scott (Scott, W. W., work cited, p. 278) says:—"This method

suggested by Chatard, has been pronounced by Brearly and Ibbotson to be one of the most stable processes found in analytical chemistry. It is not interfered with by the presence of large amounts of acetic acid, lead acetate, or alkali salts (except sulphates). The paper need not be ignited separately and prolonged ignition at a much higher temperature than necessary to destroy the paper does no harm. From faintly acid solutions lead molybdate may be precipitated free from impurities in the presence of copper, cobalt, nickel, zinc, manganese, magnesium, and mercury salts. It may be readily separated from iron and chromium. Barium, strontium, uranium, arsenic, cadmium, and aluminium do not interfere if an excess of hydrochloric acid has been added to the solution followed by lead acetate and sufficient ammonium acetate to destroy the free mineral acid. The precipitate is granular, easily filtered, and washed. Vanadium and tungsten interfere, but may be readily separated from the molybdenum."

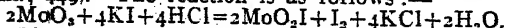
Rather (Rather, J. B., "Molybdic Acid," *Jour. Assoc. Official Agr. Chem.*, 1915, i., 317-29; 1916, ii., 39) also referred to this method.

Titration with Lead Acetate.—Titration with lead acetate is the reverse of the ammonium molybdate method for the determination of lead and has the same limitations. The colour change of the tannic acid solution is not sharp enough for use on low-grade materials.

Titration with Potassium Permanganate.—Titration with potassium permanganate comprises reducing the molybdenum solution in a Jones reductor and titrating with potassium permanganate. This is a stable process and gives accurate results. The variables are easily controlled, and the method can be used for assaying high-grade as well as low-grade material.

Titration with Titanium Chloride.—Titration with titanium chloride applies more generally to the determination of molybdenum in steel (Travers, M., "Nouveau dosage volumétrique du molybdène et du vanadium dans les aciers," *Compt. Rend.*, 1917, clxv., 362; abstract in *Eng. and Min. Jour.*, 1918, cv., 585; and *Jour. Soc. Chem. Ind.*, Oct. 31, 1917).

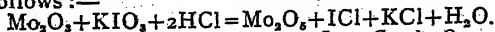
Iodometric Method.—By the iodometric method a mixture of molybdic acid and potassium iodide is boiled in the presence of hydrochloric acid, the volume having defined limits. Free iodine is liberated and expelled, and the molybdic acid is reduced to a definite lower oxide (Gooch, F. A., and Fairbanks, Charlotte, "The Iodometric Estimation of Molybdic Acid," *Am. Jour. Sci.*, series 4, 1896, ii., 160; Gooch, F. A., and Pullman, O. S. jr., "The Estimation of Molybdic Acid Reduced by Hydriodic Acid," *Am. Jour. Sci.*, series 4, 1901, xii., 449). The reaction is as follows:—



This method finds no practical application, because of the difficulty of obtaining a quantitative reduction in accordance with the above equation (Treadwell, F. P., and Hall, W. T., "Analytical Chemistry," 3rd ed., 1912, ii., 666-67).

Titration with Potassium Iodate.—In titration with potassium iodate an acid solution of the molybdenum is passed through a Jones reductor, the solution is received in a flask containing a solution of ICl in the presence of HCl, and the molybdenum is titrated with a solution of KIO₃.

The reaction (Jamison, G. S., "On the Determination of Molybdenum by Potassium Iodate," *Jour. Am. Chem. Soc.*, 1917, xxxix., 246-9) is as follows:—



Comments on Adaptability to Low-Grade Ores.—The foregoing methods were carefully studied to determine their adaptability to the determination of molybdenum in low-grade material, the length of time necessary to complete the determination always being considered. The following comments refer to the methods in the order given:—

The precipitation as sulphides was not tried out, because the method was considered too tedious and the amount of precipitated sulphides too small, as precipitated MoS₃ contains only 0.50 per cent Mo. The conversion to some weighable form also offers too many difficulties.

The precipitation as mercurous molybdate was not tried, as it offered practically the same difficulties as the preceding method.

The precipitation as lead molybdate was tried out because it seemed to offer possibilities for accurate analysis of low-grade material, as the precipitate PbMoO₄ represents 26.15 per cent Mo. Furthermore, no special precautions are necessary in igniting the precipitate.

The titration with lead acetate was tried only on low-grade material assaying less than 0.15 per cent molybdenum. The method was unsatisfactory, as the insoluble lead molybdate did not form a precipitate immediately and the end point with tannic acid was not dependable.

Many experiments were made with the method of reduction of the molybdenum and titration with potassium permanganate. This method is accurate, rapid, and adaptable to use with all the ores of molybdenum, regardless of the method of decomposition. However, it has certain well-defined variables that must be absolutely understood and controlled.

The other methods were not tried out, as the gravimetric (PbMoO₄) and the volumetric (KMnO₄) methods gave satisfactory results.

Methods of Decomposition.—Methods of decomposition that have been suggested are as follows:

Fusion with sodium peroxide (Darroch, James, and Meiklejohn, C. A., "A Rapid Method of Determining Molybdenum," *Eng. and Min. Jour.*, 1906, lxxxii., 818); fusion with sodium or potassium carbonates or mixtures of the carbonates, with a small amount of potassium nitrate present to oxidise the sulphides (Horton, Frederick W., "Molybdenum: Its Ores and their Concentration," Bull. 111, Bureau of Mines, 1916, p. 41); fusion with potassium bisulphate (Mabee, H. C., "Molybdenum Content of Ores and Concentrates," *Eng. and Min. Jour.*, 1918, cv., No. 18, 836); decomposition with aqua regia; decomposition with aqua regia followed by the addition of sulphuric acid and heating to fumes (Colett, E., and Eckhardt, M., "Bemerkungen zur Bestimmung des Molybdäns im Molybdänglanz," *Chem. Ztg.*, Jahrg. 33, 1909, xcvi., 968).

Fusion methods offer rapid and complete decomposition of the ores.

Decomposition by aqua regia is applicable to ores carrying no lead.

Decomposition by aqua regia, followed by the addition of sulphuric acid and heating to fumes, is especially applicable to ores carrying lead. This is the method used for wulfenite ores.

Volumetric (Potassium Permanganate) Method for Low-Grade Ore.

The ore is decomposed either by acid or by fusion with Na_2O_2 into a soluble molybdate and insoluble compounds of the other constituents of the ore. The molybdate is filtered, acid added, and the solution is passed through a Jones reductor where the MoO_3 is reduced to Mo_2O_3 . The Mo_2O_3 is then titrated with KMnO_4 , and the percentage of molybdenum present is calculated.

Procedure for Acid Decomposition.—Weigh out 0.5 grms. of ore, depending on its richness in molybdenum. The content of the portion taken for analysis should not exceed 0.08 grm. Mo, as explained under "Size of Sample" (*prox.*). Decompose the sample with aqua regia in an Erlenmeyer flask, heating for 15 minutes. Cool the solution, add 20 cc. of dilute (1:1) sulphuric acid, evaporate to fumes, cool again, dilute, neutralise without filtering off the insoluble matter and add 10 cc. excess of ammonium hydroxide, boil and filter and wash with hot water five times. Redissolve the precipitate into the original Erlenmeyer flask by puncturing the filter paper, washing the content into the flask and dissolving with dilute sulphuric acid. Reprecipitate, boil, filter, and wash well. The filtrate should be clear and colourless; add enough dilute sulphuric acid so that there will be present after neutralising all the ammonia, at least 12.5 cc. of free concentrated sulphuric acid for each 250 cc. of solution. The solution is now ready to be reduced by passing through the Jones reductor.

(To be continued).

REPORT FOR THE YEAR 1919
OF THE
FOOD INVESTIGATION BOARD, DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

THE Food Investigation Board beg leave to present to the Committee of the Privy Council for Scientific and Industrial Research the following Report for the year 1919.

Introduction.

The account of the work of the past year is set out in the following pages in sections relating to the various Committees of the Board into which it naturally falls. Only one research is, so to speak, extra territorial in that it comes under no particular Committee, namely, the research on accessory food factors, which has been carried out at the Lister Institute of Preventive Medicine.

These mysterious substances which exert so profound an influence upon digestion and assimilation are being intensively studied by a Committee specially appointed for the purpose, by the Medical Research Council and the Lister Institute. Arrangements have been made whereby the Board will be kept in close touch with the work of that Committee so that results of importance to industry may be included in the publications of the former. In the meantime, Dr. A. Harden, F.R.S., of the Lister Institute, has completed a prolonged investigation of the effect of cold storage upon that accessory food factor which occurs in butter

and is known either as the "growth factor," or as "fat soluble A." By the courtesy of the Colonial Consignment and Distributing Company, Ltd., butter was kept in their stores at Nelson's Wharf, Lambeth, for twelve months at -8° to -15° C., and the content of fat soluble A determined at the close of the period. There was no material loss. Cold, therefore, preserves this accessory food factor completely. This result is of considerable scientific importance, as it makes it possible to study the influence upon the quantity of vitamin present in milk or butter, of the diet of the animal, and of the season of the year.

Dr. Harriette Chick has continued her investigation of the effect of cold storage upon the accessory food factors of fruits, and especially of the factor the absence of which from the diet causes scurvy.

The greater part of the research work has, during the year under survey, been devoted directly or indirectly to the preservation of food by cold. Though there are many ways of maintaining food in a state fit for human consumption, there is none so far which preserves its nutritive properties so completely as does cold.

Of the three Committees which between them cover this field the work of the Engineering Committee differs from that of the Fruit and Vegetables Committee and the Meat Committee in its more immediate relation to practice. Determinations of the properties of insulating materials, and experiments in the equipment and construction of refrigerated barges, come right up to the day-to-day needs of industry.

The work of the other two Committees, on the contrary, for the most part consists in an attempt to increase our knowledge of the chemistry of the ripening fruit, or of the post-mortem changes in animal tissues. It is laboratory work concerned with the fundamental science of living matter, and the applicability to industry of many of the researches is not immediate and often not obvious.

This is not due to deliberate intent on the part of either Committees or research workers. It is the natural result of the state of development of the sciences concerned.

Engineering is an old science. Much of the abstract work on heat engines and on heat flow was done nearly a century ago. We are now in the period of refinements of knowledge, and the application of principles established long since to special problems. Biochemistry is a young science—as it is understood now it is ten or twenty years old at the most. It is rapidly growing, but the fundamental knowledge, enormously more complex than that of the engineer, is yet far from clear. The Meat Committee and the Fruit and Vegetables Committee have at their command only this partially developed science. If their work is to be thorough, therefore, it must go deep.

Investigations of this kind are of no use unless they are as exact as the methods available permit of. To carry them out properly it is necessary to have a laboratory specially equipped for the purpose where not only the different modes of applying cold may be tested but also where the material which has been specially treated may be kept under observation for many months. Up to the present the Board have had to rely upon a small installation containing only six small chambers, or rather cupboards, placed at their disposal

by the kindness of the Professor of Pathology at Cambridge. This plant has had to serve for continuous observations on moulds, on fish bacteria, on frozen meat, and on fruit. Months of work would have been lost if the temperature had got out of control at any time during the year, and the Board gladly recognise the fact that this small plant has served their workers so well owing to the devoted and anxious service of the Secretary of the Meat Committee, Mr. L. F. Newman.

So small an experimental store is totally inadequate except for experiments on the smallest possible scale. It has, however, been invaluable in providing the Board with the experience necessary for the design of an experimental store fit for their work. Indeed without the experience gained during the last eighteen months it would have been impossible to design such a store. Having gained the necessary experience the Board have applied for a grant of money sufficient to build an experimental Low Temperature Research Station fully equipped for biochemical and biophysical investigations at low temperatures. The application has been granted and the University of Cambridge have presented a site for the erection of the station in close proximity to the Departments of Biochemistry, Animal Nutrition, and Botany.

The investigations carried out by the Board range so widely as to render it difficult effectively to summarise them. They deal with the engineering problems of the cold storage industry, with the preservation by cold and by canning of fish, meat and fruit, with the chemistry of putrefaction, and the agents which bring it about, with the bionomics of moulds, and with the chemistry of edible oils and fats.

Probably the chief needs of the fishing industry at the moment are improved methods of transport and the development of a mode of preservation capable of dealing with the excess fish landed during gluts. The Engineering Committee of the Board produced last year a report dealing with the construction of refrigerated wagons suited for this country, and the Fish Preservation Committee have just completed a report, now in the Press, upon the use of fish freezing in times of glut, based upon experiments carried out mainly at Billingsgate Market and University College, London.

The Meat Committee have completed experiments upon the freezing of beef. It is a remarkable fact familiar to the industry that whereas mutton can be frozen without damage, beef cannot. The effect of freezing on the latter is so to alter the muscle substance as to cause the meat, on thawing, to exude a fluid rich in nutritive material and coloured with hæmoglobin. The new experiments prove that, provided certain precautions are taken, beef can be frozen in such a way as to preserve completely the physical and chemical qualities of the fresh meat. The experiments were carried out with small pieces of beef, and the attempt to repeat them on a commercial scale has so far failed for want of adequate apparatus. Further investigations have been postponed until the Research Station referred to above is completed.

The work on putrefaction has been devoted to an analysis of the factors which determine the rate of multiplication of bacteria and limit their activities. It appears that for each species of

bacteria, the rate of growth and the cessation of growth are determined by the quantity of some foodstuff which is specific for each species. The anaerobic spore-bearing bacilli have been specially investigated. The study of this important group has been hampered in the past by the difficulty experienced in cultivating more than a small proportion of those shown to be present by microscopical methods. A culture medium has now been found in which these organisms grow freely. The methods commonly used for estimating the chemical changes produced by bacteria, or enzymes, have hitherto been so laborious as to render it almost impossible to make observations rapidly enough to follow the rate and order of these changes. New methods have therefore been devised for estimating the simple products of decomposition which are both easy and accurate.

Considerable progress has been made towards the completion of a monograph of the moulds which grow on cold-stored meat, and special attention has been given to the "black spot infection" of beef and mutton. It is now clear that this trouble is due solely to one or more species of *Cladospodium*, a genus of world-wide distribution, the members of which grow chiefly upon dead vegetable tissues. Although there has been a belief in the trade for some time that certain of these moulds would develop under cold-store conditions, there has always been some doubt as to whether these growths were not due to some temporary breakdown of the plant during storage, either on board ship or elsewhere. It was, therefore, important to perform critical experiments to ascertain whether any of these fungi would develop under uniform cold-store conditions. This has been done, and it has been shown conclusively that the fungus causing "black-spot" will grow and produce spores at a temperature at least 5° C. below freezing point. So far, the "black-spot" fungus is the only one found to grow at a temperature considerably below 0° C., but several others develop fairly well at freezing point. Experiments are being made upon the vitality of spores kept under cold-storage conditions for various periods.

Experiments have proved that dried blood added in small amounts to the diet of pigs produces a remarkable increase in the rate of fattening.

Mention was made earlier of the work of the Engineering Committee on the design of refrigerated railway wagons. The Committee have now in hand experiments directed to securing the design of refrigerated barges best suited for transferring produce from ship to store. A steel motor-driven barge is being fitted for the purpose, and will be completed for service during the hot months of the year.

An apparatus of novel design for the measurement of the heat-flow through materials has been installed in triplicate at the National Physical Laboratory, and all the substances commonly used in insulation have now been tested. Considerable attention has also been given to the loss of heat by convection from plane surfaces, as practically nothing is known concerning the laws which govern it. Loss of heat by radiation has also been investigated especially in connection with the effect upon it of the nature of the radiating surface.

Experiments on hygrometry at low temperatures are in progress at the National Physical Laboratory and at the Physical Laboratory of the University of Bristol.

Experiments on the storage of fruit have shown that by the employment of certain artificial atmospheres in the storage chambers, the life of the fruit may be greatly extended. A method of drying certain fruits which promises good results has also been worked out. The study of the respiratory metabolism of fruit at low temperatures, and of the oxidising enzymes responsible for the discoloration of certain fruits on injury has also been continued. The chemistry of the ripening process in fruit has been investigated with special reference to the changes in the pectin, and the limits of temperature within which the moulds commonly infest fruit in store will grow have been determined.

The work of the Oils and Fats Committee consists, in part, of investigations begun during the war at a time when there was the possibility of an acute conflict between the demands for oils and fats for human consumption on the one hand, and for the preparation of the glycerol needed for the manufacture of explosives on the other. A process has been discovered which points to a successful synthesis of glycerol, and the physiological properties of fats in which glycerol has been replaced by other polyhydric alcohols have been determined. Experiments have been made on the production from linseed oil of an edible oil. The production of oils by vegetables has been studied, and an important monograph of the unsaturated monobasic acids related to fats has been completed.

The Canned Foods Committee have completed a report, which is now in the Press, on the methods of inspection of tins, and are continuing their work on the bacteriology and chemistry of canned foods.

Fish Preservation Committee.

Work under this Committee has not been on a scale commensurate with the importance of the subject, owing to the fact that the only plant available for experiments has been a small brine freezing plant, installed originally for demonstration purposes in the basement of Billingsgate Market. Two research workers, Mr. G. Adair and Mr. J. Piqué, made experiments upon the rate of freezing fish in cold brine, upon the penetration of salt into the bodies of brine-frozen fish, and upon certain mechanical devices designed for the application of the process of freezing in brine to commercial practice. They made full use of the plant during the many months they worked there, until the total absence of daylight, the damp and the noise made them both seriously ill. The experiments at Billingsgate were supplemented by others carried out in the Physiological Laboratory of University College, London, by the kindness of Professor W. M. Bayliss, F.R.S.

In spite of difficulties, to which no description can do justice, Mr. Adair and Mr. Piqué have carried their investigations far enough to form the basis of an interim report upon the freezing of fish, which the Committee are now completing.

In addition to the work at Billingsgate, Miss I. H. Green has been engaged upon an intensive study of the bacteria which occur in herring. She has isolated, cultivated, and identified many species, and by so doing has laid a foundation for the further study of putrefactive change in these fish. In June, 1919, Miss Green visited North Shields, where, by the courtesy of Mr. George Wilson, of the Shields Ice and Cold Storage Company, she was able to make a special study of the bacterial changes in herring which had been treated in various ways. The chief results at which she arrived were:—

- (1) That the number of bacteria present in herrings which have been frozen in brine is less than that in herrings frozen in air. The cold brine appears to kill many of the bacteria before they have time to spore;
- (2) That the keeping properties of ungutted herring are greater than those of gutted herring.

(To be continued).

INSTITUTE OF METALS.

A PROGRAMME of the intended meetings and of the work of the various local sections for the Session 1920-21 has been issued. The work of the Institute is of the greatest importance at the present time, and the following list of lectures arranged under the Presidency of Vice-Admiral Sir George Goodwin, K.C.B., LL.D., speaks well for the vitality of the Institute.

General Meetings.

- March 9. Annual General Meeting, 10.30 a.m.
Annual Dinner.
March 10. Annual General Meeting, 10.30 a.m.
May 4. Annual May Lecture, 8 p.m., by
Prof. T. Turner, M.Sc., A.R.S.M.

Birmingham Local Section.

- October 12. H. W. Brownsdon, M.Sc., Ph.D.
Chairman's Address.
November 16. Discussion upon "Hardness in Non-ferrous Alloys."
December 14. W. R. Barclay, O.B.E. "Some War Experience in the Electro-deposition of Metals."
January 11, 1921. Ernest A. Smith, A.R.S.M. "Segregation in Non-ferrous Alloys."
February 15, 1921. O. F. Hudson, D.Sc. "Bearing Metals."
March 22, 1921. R. T. Rolfe. "Gun Metal."

Sheffield Local Section.

- October 15. Ernest A. Smith, A.R.S.M. "The Development of Non-ferrous Research." (Chairman's Address).
November 19. "Electroplating." (Conjoint Meeting with the Faraday Society).
December 17. J. Kent Smith, O.B.E. "Some Alloys in the Foundry."

- January 28, 1921. Prof. C. H. Desch, D.Sc., Ph.D. "60:40 Brass."
 February 18, 1921. F. Rogers, D.Eng., B.A., M.Sc. "Cracking in Worked Brass and other Metals."
 March 18, 1921. W. Rosenhain, D.Sc., F.R.S. (Vice-President). "The Crystal Boundary."
 April 15, 1921. H. A. Greaves. "A New Non-ferrous Electric Furnace."

Scottish Local Section.

- October 27. The Rt. Hon. Lord Weir of Eastwood, P.C. (Member of Council). Address on "Some Notes on Foundries and Production."
 November 9. J. A. C. Edmiston. "Fuel."
 December 14. Discussion on "Furnaces" (to be opened by Messrs. J. Stirling and J. Arnott).
 January 11, 1921. S. E. Flack. "Rolling and Extrusion."
 February 8, 1921. G. H. Bailey, D.Sc., Ph.D. "Aluminium, Production and Uses."
 March 8, 1921. Annual General Meeting. Address by Mr. James Steven (Vice-Chairman, Local Section).

NOTES.

BIRMINGHAM UNIVERSITY AND RESEARCH.—Towards the appeal for £500,000 to maintain and develop the work of the University of Birmingham (which was formally inaugurated on Thursday last), £200,000 was promised. Mr. Austen Chamberlain, the Chancellor of the University, stated that the Government had this year given a million pounds to the Universities. He hoped they would be able to increase the amount next year by half-a-million. The Government recognised fully the splendid services rendered during the war by the Universities, and particularly on the Science side. The Government were prepared to back their opinion of the importance of University work. The Principal, Mr. Grant Robertson, declared that a University which was not carrying on research was a crippled educational organisation. Research paid. It gave a dividend in cash, and it paid ultimately in a general and heightened national efficiency. He believed that if more money had been put into the Universities for the ten years preceding 1914, that the war would have been shortened by two years.

BOARD OF TRADE ANNOUNCEMENT.—Mr. L. G. Kilby has been appointed Secretary to the Empire Cotton Growing Committee. He is at present Superintendent of the Department of Technology, City and Guilds of London Institute. In 1904 at Oxford, he took his B.A. degree in the Honours School of National Science, with 1st Class Honours in Chemistry. He then became Demonstrator in Chemistry, and in 1907 was awarded the degree of B.Sc. (Oxon) for research work. He has been on the staff of the Department of Technology for 14 years. During the war Mr. Kilby received a commission in the Army, and served in France as one of the chemists on water supplies in the Field, and was afterwards transferred to the Chemical Warfare Department of the Ministry of Munitions. He was mentioned in dispatches.

THE FARADAY SOCIETY AND THE PHYSICAL SOCIETY OF LONDON.—A General Discussion on "The Physics and Chemistry of Colloids and their Bearing on Industrial Questions" will take place on Monday, October 25. The following is the programme:—

2.30 to 4. General Introduction "A Short Survey of the Physics and Chemistry of Colloids," by Prof. Dr The Svedberg, of the University of Upsala.

Discussion on "Emulsions and Emulsification." Opener: Professor F. G. Donnan, C.B.E., F.R.S. Mr. W. Clayton, M.Sc. will read a paper on "Emulsion Problems in Margarine Manufacture." Mr. S. S. Bhatnagar will read a paper on "Reversal of Phases in Emulsions and Precipitation of Suspensions by Electrolysis—an Analogy."

4.30 to 6.15. Discussion on "Physical Properties of Elastic Gels." Openers: Mr. E. Hatschek, F.Inst.P., and Prof. H. R. Procter, D.Sc. Mr. S. C. Bradford will read a paper on "The Reversible Sol gel Transformation." Dr. J. O. W. Barratt, M.D., D.Sc., will read a paper on "The Structure of Gels."

Discussion on "Glass and Pyrosols." Opener: Sir Herbert Jackson, K.B.E., F.R.S.

8 to 10. Discussion on "Non-Aqueous Systems."

(a) Nitrocellulose. Opener: Sir Robert Robertson, K.B.E., F.R.S. Mr. F. Sproston will read a paper on "Non-aqueous Colloid Systems with special reference to Nitrocellulose." Dr. Guy Barr and Mr. L. L. Bircumshaw will read a paper on "The Viscosity of some Cellulose Acetate Solutions." (b) Rubber. Opener: Mr. B. D. Porritt, speaking on "The Action of Light on Rubber."

Discussion on "Precipitation in Disperse Systems." Openers: Dr. R. C. Tolman and Dr. R. S. Willows. Mr. J. N. Mukherjee, M.Sc., will read a paper on "The Origin of the Charge of a Colloidal Particle and its Neutralisation by Electrolytes." Mr. W. Clayton, M.Sc., will read a paper on "Coagulation of Inorganic Suspensions by Emulsions."

Discussion on "Cataphoresis and Electro-Endosmose." Opener: Professor A. V. Porter, D.Sc., F.R.S. Dr. W. R. Ormandy, F.I.C. will read a paper on "Some Practical Applications of Electro-Endosmose and Cataphoresis."

The Secretary of the Department of Scientific and Industrial Research begs to announce that a license, under Section 20 of the Companies' (Consolidation) Act, 1908, has been issued by the Board of Trade to the British Electrical and Allied Industries Research Association, which has been approved by the Department as complying with the conditions laid down in the Government scheme for the encouragement of industrial research. The Association may be approached through E. B. Wedmore, Electrical Research Committee, c/o Electrical Development Association, Hampden House, 64, Kingsway, W.C.2.

MAGNESITE AND SHELL-MAKING.—During the war magnesite was found useful in the manufacturing of shells, and now the *Engineering and Mining Journal* of New York reports that Mr. H. F. Weirum has been experimenting with ground magnesite as a substitute for lime in making egg shells. He finds that hens fed on the ground magnesite produce a very superior grade of shell. Apparently the old bone-grinding machine used so often in hen yards will soon have to give way to packages of magnesite. As the *Canadian Mining Journal* says in reference to the matter. It is another example of how the old-established industries have been helped by the hunt for substitutes.

DEVELOPMENT OF ALCOHOL FUEL.—The Empire Motor Fuels Committee of the Imperial Motor Transport Council is dealing actively with the general conditions underlying production and development of alcohol for power and industrial purposes. It has recently appointed small Expert Committees to deal with: (a) The modification of Customs and Excise Restrictions in connection with alcohol; (b) By means of experiments, the best conditions for developing the alcohol engine and types of alcohol fuels—alone or in mixture—for the purpose; and (c) The very important subject of denaturation (or rendering alcohol unpotable). Good progress is being made with the work of all three Committees, but it is felt that members of the public who may have given special attention to the question of denaturation of alcohol should be invited to forward any suggestions for confidential examination and report by the Denaturation Committee. Any such communications should be addressed to Sir Charles Bedford, LL.D., D.Sc., Empire Motor Fuels Committee, 50, Pall Mall, London, S.W.1., marked "Denaturation," and will be treated as strictly confidential. Any suggestions which may prove practicable will remain the sole property of the proposer. It is essential that any proposals regarding denaturants should be made with the knowledge of the particular requirements of a satisfactory denaturant, viz.: (a) Deterrent taste and smell; (b) Non-poisonous; (c) Must not be removable at a commercial cost; (d) Must be readily detectable in small quantities; (e) Must be readily mixable with the spirit; and (f) Must be inexpensive. It is, of course, exceedingly difficult to obtain any one substance which will conform to all these requirements, but the difficulty in practice has usually been overcome by using a combination of substances whose complementary action meets the requirements. It is inevitable that many suggestions will be made which fail to meet these requirements, but it is believed that a successful object will be attained by letting those interested know that there exists a small expert body, *acting solely in the public interests*, which is prepared to examine confidentially any proposals regarding denaturants. In the event of any such suggestions proving workable, the inventor would be communicated with, and his interests fully safeguarded before proceeding to communicate the results to the Empire Governments concerned.—F. G. Bristow, Hon. Secretary, 50, Pall Mall, S.W.1.

GREY AND MALLEABLE CAST IRON TRADE.—On Thursday, September 30, the British Grey and Malleable Cast Iron Research Association was

formally brought into being at a largely attended meeting of ironfounders from all parts of the country, metallurgists, and industrial chemists. The headquarters are in Birmingham, and Mr. T. Vickers, C.E., Lincoln's Inn, Birmingham, is the Secretary. This is the second research association founded in Birmingham under the Government scheme, the other being in connection with non-ferrous metals. Sir Frank Heath, K.C.B. (Government Department for Scientific and Industrial Research) explained the objects of the Association, mentioning that there are 2,796 iron foundries in Great Britain and Ireland, that the largest single county foundry area is Yorkshire with 408, and the largest single town foundry area is Birmingham with 118 foundries. The application of science to industry said Sir Frank Heath, was really nothing more than an insurance against the evil effects of ignorance. The first incentive to new ways for competition they got from America. A research association founded in the United States had given promising results, and it was claimed they could make malleable castings of more than 50 per cent tensile strength than was possible in this country. Competition was, however, really nearer, for he learned that in Scotland there was an association of light castings manufacturers who had established a research laboratory. There was nothing corresponding to this south of the Tweed. It was essential that we should know precisely the quality and characteristics of pig-iron, and the proper constitution of the metal from which the casting was to be made. These were matters for scientific investigation. It was decided to form a Grey and Malleable Cast Iron Research Association, on the motion of Dr. L. Aitchison and Prof. T. Turner, University of Birmingham, and representing the Birmingham and Midland Section of the Society of Chemical Industry, pointed out that there were wide fields for research. It was not merely a question of the chemical composition of pig-iron, the effects of different rates of cooling, or impurities in melting, but also the effect of pressure during casting, the composition of sand, and the texture of sand apart from composition, and the amount of blast employed.

MANCHESTER COLLEGE OF TECHNOLOGY WAR MEMORIAL.—The War Memorial Committee, representing all present members of the College, graduate and undergraduate, propose to preserve in the College a permanent memorial which shall include the names of all former students of the College who were killed or who died on service during the late war. The provisional list, which is under amendment, comprises nearly one hundred names.

MEETINGS FOR THE WEEK.

Monday, October 25.

Faraday Society and Physical Society, 2.30. (At Institution of Mechanical Engineers). Discussion: "Physics and Chemistry of Colloids and their Bearing on Industrial Questions."

Wednesday October 27.

Conjoint Board of Scientific Societies, 5. (Board Meeting).

Thursday, October 28.

Chemical Society, 8. "Fischer Memorial Lecture" by Dr. M. O. Forster, F.R.S., at the Lecture Hall of the Institution of Mechanical Engineers.

NOTICES.

EDITORIAL.—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the Editor.

SUBSCRIPTIONS, £1 18s. per annum, payable in advance, should be addressed to the MANAGER.

BACK NUMBERS and **VOLUMES** can be purchased on application to the MANAGER.

THE CHEMICAL NEWS,
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ADVERTISEMENTS.

All communications for this Department should be addressed to—

T. G. SCOTT & SON,
63, LUDGATE HILL, LONDON, E.C.4.

**MUNICIPAL TECHNICAL COLLEGE
SWANSEA.**

Acting Principal—T. GILBERT JONES, M.Sc., Wh.Sc., A.M.I.C.E.

LECTURESHIP IN PHARMACY.

APPPLICATIONS are invited for the above lectureship. Salary £400 per annum. The appointment is a whole-time one in the Chemistry Department of the College. The lecturer will be briefly required to give instruction in Pharmacy and Materia Medica to students preparing for the Professional Examinations of the Pharmaceutical Society of Great Britain, but qualifications in Botany and Chemistry are desirable. Applications, stating age and particulars regarding training qualifications and experience, accompanied by copies of testimonials to be sent to the undersigned not later than Monday, November 1st.

T. J. REES, B.A.,
Director of Education,
Education Offices,
Swansea.

11th October, 1920.

LEEDS UNIVERSITY.**DEPARTMENT OF COLOUR CHEMISTRY
AND DYEING.**

THE Council will shortly proceed to the appointment of a Lecturer and Research Chemist in Colour Chemistry and Dyeing, at a salary of £450 a year. Preference will be given to a candidate with some works experience. Applications should be sent to THE SECRETARY, The University, Leeds, from whom further particulars may be obtained.

DEVON COUNTY COUNCIL.

THE Agricultural Committee invite applications for the post of Assistant Agricultural Analyst and Lecturer in Agricultural Chemistry.

The salary offered is £350 per annum. Further particulars and forms of application may be obtained from:—

The Agricultural Organiser,
F. V. DUTTON,
1, Richmond Road,
EXETER.

ESSEX EDUCATION COMMITTEE.

**EAST ANGLIAN INSTITUTE OF AGRICULTURE,
CHELMSFORD.**

**WANTED, an ASSISTANT LECTURER
in AGRICULTURAL CHEMISTRY.**

Salary £350 per annum rising by annual increments of £20 to £450.

Applications must be made in accordance with the printed application form, which can be obtained from the undersigned.

These, together with copies of three recent testimonials, must reach me by Monday, October 25, 1920.

R. M. WILSON, Principal.

ESSEX EDUCATION COMMITTEE.

**EAST ANGLIAN INSTITUTE OF AGRICULTURE,
CHELMSFORD.**

WANTED an ASSISTANT ANALYST.

Salary £350 per annum, rising by annual increments of £20 to £450.

Applications must be made in accordance with the printed application form, which can be obtained from the undersigned. These, together with copies of three recent testimonials, must reach me by Friday, October 29th, 1920.

R. M. WILSON, Principal.

**THE
QUEEN'S UNIVERSITY OF BELFAST****LECTURESHIP IN ORGANIC CHEMISTRY.**

APPPLICATIONS are invited for the Lectureship in ORGANIC CHEMISTRY, which is now vacant.

Information as to TERMS OF APPOINTMENT may be obtained from:—

J. M. FINNEGAN,
Secretary.

BOOKS.—The following second-hand volumes, mostly bound, are offered for sale. Full details on application to Hon. Secretaries, 36, GEORGE STREET, MANCHESTER. *Amer. Chem. Soc. Journal*, vols. 31-41; *Chem. Abstracts*, vols. 3-12. *Chem. News*, vols. 47-109, 111-115, 116-119 (incomplete). *J.C.S.*, vols. 15-22, 24-46, 48-114, and 57-63, 93-98. *Proc. C.S.*, 1896-1908. *Ann. Rept. Prog. Chem.*, vols. 1-5, 5-8, 12-15. *J. Soc. Chem. Industry*, vols. 30-32. *Alkali Inspector's Repts.*, 1864-1914.

THE Council of The Linen Industry Research

Association are desirous of appointing a Senior Research Physicist and an Assistant Research Physicist to conduct work of a physico-chemical and physical nature in connection with the Linen Industry. According to qualification for the position the remuneration offered will be about £700 and £400 respectively. Application Forms may be had on application to the SECRETARY, Research Institute, Lambeg, Belfast.

CHEMIST wanted with experience in taking charge of Caffeine Plant and other fine Chemicals.—Reply Box 815, c/o SCOTT & SON, 63, Ludgate Hill, E.C.4.

KIESELGUHR (DIATOMITE). All grades for every purpose always in stock at principal ports. A. EGGERMONT, Victoria Chambers, Middlesbrough-on-Tees.

PATENTS, TRADE MARKS. Handbook and advice free—B. T. KING, British and U. S. Regd. Patent Attorney, 146a, Queen Victoria St., London. 35 years reference.

FOR Sale.—Filter-press, by Manlove Alliott; practically new; centre feed, with pressure pump; offers invited.—CANNINGS, Salop Street, Highgate Birmingham.

If in good condition, Sixpence per copy will be paid for any of the undermentioned numbers of the **CHEMICAL NEWS** which may be forwarded to this office:—

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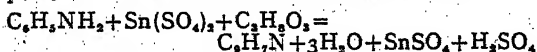
THE CHEMICAL NEWS.

VOL. CXXI., No. 3159.

A MODIFICATION OF SKRAUP'S QUINOLINE SYNTHESIS

By EDWARD DE BARRY BARNETT, B.Sc., F.I.C.

THE yield of quinoline obtained when aniline is heated with nitrobenzene, glycerine, and concentrated sulphuric acid (Skraup, *Monatshefte*, i., 317, ii., 141; Walter, *J. pr. Chem.* [2] xlix., 549) is about 50 per cent. of that theoretically possible when calculated on the aniline used, but is only about 27 per cent of that theoretically possible with regard to the glycerine. The use of arsenic acid as an oxidising agent in place of nitrobenzene (Kneuppel, *B.*, xxix., 709; *D.R.P.*, lxxxvii., 334) although it leads to somewhat increased yields with reference to the aniline is even more extravagant in glycerine, as only about one-fifth of that used enters into the reaction. More recently, Druce (*CHEMICAL NEWS*, 1917, cxvii., 346) has described the preparation of quinoline from aniline stannichloride, glycerine, and sulphuric acid, and has stated that 50 grms. of aniline stannichloride yield 20 grms. of quinoline. These figures correspond to a yield of 80.5 per cent of that theoretically possible with reference to the aniline present in the stannichloride. The formation of a molecule of quinoline, however, requires the oxidising powers of a whole atom of tetravalent tin:—



and consequently Druce's result is difficult to understand, as calculated on the tetravalent tin present in the stannichloride his yield is 161 per cent of that theoretically possible. It seemed superfluous to prepare the stannichloride and then to treat it with sulphuric acid, but a few experiments were made in which aniline was heated with glycerine, sulphuric acid, and stannic sulphate. These resulted in yields of quinoline corresponding to about 30 per cent of the theoretical provided only about the calculated amount of glycerine was used. If, on the other hand, a large excess of glycerine was employed, as in the experiments described by Druce, the yields of quinoline were very poor. The experiments with stannic sulphate were abandoned, however, as it was found that much better results were obtained when the cheaper ferric sulphate was employed. Even with this oxidising agent, however, yields exceeding 60 per cent of theory could not be obtained, and it seemed probable that the relatively poor yields were due to the destruction of the glycerine before quinoline formation had had time to take place. Experiments were therefore carried out in which (a) a great excess of glycerine was employed; (b) the glycerine was slowly dropped into a heated mixture of aniline, ferric sulphate, and sulphuric acid; (c) the reaction was carried out at 130°; (d) the sulphuric acid was diluted to 80 per cent strength. None of these modifications, however, resulted in any definite improvement in the yield. Experiments were also made in which an excess of boric acid was added in the hope that a boric

ester would be formed which would not be so readily destroyed by the sulphuric acid. This method has been very successfully used for the protection of hydroxyl groups during the preparation of hydroxyanthraquinones by direct oxidation (Bayer & Co., *D.R.P.*, lxxix., 768; lxxxii., 244; lxxxii., 481; lxxxii., 956; lxxxii., 960-1-2, etc.), but in the case of quinoline formation the boric acid seemed to have no effect at all. It is probable therefore, that the relatively poor yields obtained are due not so much to the destruction of the glycerine as to the destruction of the aniline, and, in fact, it was found that aniline is fairly easily destroyed when heated with ferric sulphate and sulphuric acid at 140°.

When stannic sulphate was used as an oxidising agent the best results were obtained when aniline (50 grms.) was added to concentrated sulphuric acid (75 cmm.), the solution cooled and then the glycerine (50 grms.) and stannic sulphate (190 grms.) added. After heating on an oil-bath at 180-190° for six hours, the melt was poured into water, unchanged aniline destroyed by the addition of sodium nitrite, the solution made alkaline, and the quinoline distilled off with steam. The yields obtained were about 30 per cent of the theoretically possible. In one or two experiments in which a large excess of glycerine (150 grms.) was used, hardly any quinoline was obtained. Much more satisfactory results were obtained when ferric sulphate was used as an oxidising agent, and in fact, it was found that the use of this oxidising agent provides by far the most convenient method of preparing quinoline in the laboratory, as the very violent reaction which often takes place when nitrobenzene or arsenic acid is used is completely absent, and no tar is formed. It is unnecessary to employ dry ferric sulphate, as ordinary calcined ferric oxide, which has been previously treated with sufficient concentrated sulphuric acid to convert it into the sulphate, gives equally good results. The following procedure was found to give yields of quinoline of 45 to 50 per cent of the theoretical.

One hundred grms. of aniline was dissolved in 150 cmm. of concentrated sulphuric acid, and the solution thus obtained added to 450 grms. of dry ferric sulphate, or to 180 grms. of calcined ferric oxide, to which 370 cmm. of concentrated sulphuric acid had been added an hour or two previously. One hundred grms. of glycerine were then added, and the whole heated for six hours on an oil-bath at 180-190°. Without cooling, the melt was then poured into water, made alkaline with caustic soda, and the quinoline and unchanged aniline distilled over with steam. The distillate was then made acid with hydrochloric acid, and aniline destroyed by adding sodium nitrite. After boiling for a few minutes, so as to destroy the benzene diazonium chloride, the solution was again made alkaline and distilled with steam. The quinoline was extracted from the distillate by shaking with benzene, the extract dried over solid, finely powdered caustic soda, and the benzene then removed by distillation.

A very rapid modification of the above process which gives somewhat better yields, about 60 per cent of the theoretically possible, consists in mixing 50 grms. of aniline with 65 grms. of glycerine, and 100 grms. of calcined ferric oxide, and then adding this mixture as quickly as possible to 150

comm. of concentrated sulphuric acid in an evaporating basin. A brisk reaction sets in almost at once, and while it lasts, the mixture is kept well stirred. When the reaction subsides, the whole is allowed to stand for half-an-hour without heating, and is then poured into water and worked up as before. Several hundred grms. of quinoline have been prepared by this method which has been found to give very satisfactory results.

Both ferrous sulphate and stannous sulphate are very readily oxidised by atmospheric oxygen, so that it seemed probable that a catalytic process might be devised for the preparation of quinoline. Experiments have shown that this assumption was correct, although the reaction is somewhat slow, probably owing to the insolubility of the catalyst. In carrying out the catalytic process, it is necessary to select conditions such that the glycerine is not rapidly destroyed by the sulphuric acid, and it was found that this could be done by diluting the acid to 80 per cent strength, and then working at a temperature of 130-140°. A trace of either ferric sulphate or stannic sulphate can be used as a contact substance, but the latter is the more satisfactory. Owing to the slowness of the reaction, the process is not convenient for laboratory use, but indications were found which pointed to satisfactory results being obtained if the reaction was carried out in a closed vessel, using oxygen under pressure. The process would probably be a convenient one to use on the large scale should any demand for synthetic quinoline derivatives arise.

RUBBER SEED OIL.

FROM time to time in recent years references have been made made to the possibility of extracting the oil from the seeds of the Para rubber tree. Experiments have been made, both in this country and in the Federated Malay States, and the results were such as to encourage those who claimed that the seeds had a commercial value. At first it was believed that rubber seed oil would prove a substitute for linseed oil; but as yet this belief has not been substantiated, though doubtless further experiments by the chemists may bring about developments which may make it worth while for the planting companies to collect the seeds for the sake of the oil they contain.

In his report on the Agricultural Department of the Federated Malay States in 1919, just to hand, the Director of Agriculture (Mr. L. Lewton-Brain) states that the experimental hydraulic oil-expression plant of the Department has been lent to the Malayan Oil Mills, Ltd., a local company formed primarily to manufacture rubber seed oil. It has been ascertained that seed on storage deteriorates and produces an oil containing up to about 25 per cent free fatty acids, and that such oil is not generally suitable as a substitute for linseed oil. Further, this oil is not suitable for many purposes owing to its slower drying power, compared with linseed oil, and it is necessary to prepare a "boiled" oil for commercial purposes.

Considerable progress has been made in the work of refining the oil, but it is probable that the processes required can only be carried out in a factory under the supervision of a trained chemist.

Experiments on the preparation of "boiled" oils have shown that a satisfactory product can be obtained from a raw oil free from fatty acids.

A further problem, namely, the prevention of the deterioration of seed on storage, remains to be attacked. Freshly collected seed yields an oil with very low acid content.

DETERMINATION OF MOLYBDENUM.

By J. P. BONARDI and EDWARD P. BARRETT.

(Continued from p. 199.)

Interfering Elements.

THIS method of solution by digesting with aqua regia, adding sulphuric acid and evaporating to fumes, and then boiling with ammonia, brings all the molybdenum into solution. The residue rarely, if ever, contains molybdenum. Nitric acid used in place of aqua regia in combination with sulphuric acid taken to fumes will also give excellent results. Either of these two methods will completely dissolve the molybdenum in molybdenite and wulfenite ores, and also in ferro-molybdenum if ground sufficiently fine. The silica, iron, alumina, lead, and other sulphates and insoluble matter will be found in the precipitate.

Copper and arsenic, if present, can be removed by adding several grms. of zinc to the acid solution before passing it through the reductor, where some of the arsenic is evolved as arsine. The copper when precipitated by the zinc will also precipitate the remaining arsenic. If much arsenic is present, the addition of a few cc. of a 10 per cent solution of copper sulphate may be necessary. Antimony, if present, acts in a manner similar to arsenic.

Procedures for the separation of molybdenum from tungsten and vanadium are given in standard works listed in the bibliography at the end of this paper. When vanadium is present in the ore—for example, wulfenite occurring with vanadinite, as it often does—the vanadium can be determined volumetrically by titration with the permanganate solution, as described by Scott (W. W. Scott, "Standard Methods of Chemical Analysis," 2nd ed. rev., 1917, p. 282). Vanadium can also be determined by the rapid method of reduction with HCl, in which arsenic or molybdenum do not interfere. This method is described by Moore and Kithil (R. B. Moore, and K. L. Kithil, "A Preliminary Report on Uranium, Radium, and Vanadium": *Bull.* 70, Bureau of Mines, 1914, p. 90).

Molybdenum may be precipitated as the sulphide from slightly acid solutions by passing H₂S under pressure into the solution, as described fully in standard text-books and in the references given in this paper. The addition of 2 grms. of tartaric acid will prevent precipitation of vanadium and tungsten along with the molybdenum. The same procedure may be applied to ammoniacal solutions, but the solution must be made slightly acid before the molybdenum will precipitate as the sulphide. The molybdenum sulphide may then be redissolved in strong nitric acid, fuming with sulphuric acid as previously described. Any copper sulphide liable to precipitate with the molybdenum sulphide does not interfere with the volumetric method, but does with the gravimetric sulphide method of determination.

Decomposition by Fusion with Sodium Peroxide.—Decomposition by fusion with sodium peroxide is practically the same procedure for preparing the solution of molybdenum that is used by one of the largest producers and refiners of molybdenum ores and products in this country. This method has proved fairly accurate for determining molybdenum in low-grade materials, and a complete determination can be made in 30 minutes.

Procedure.—Weigh out a 0.5 to 5 gm. sample, according to the grade of the ore; the content of Mo should not exceed 0.15 gm., as explained under "Size of Sample" (*prox.*). Place the weighed sample in a 60-cc. iron-spun crucible and thoroughly mix with six times as much sodium peroxide. Cover the crucible with an iron lid, and heat in an electric muffle maintained at a temperature of about 600° C., or in the flame of a Meeker burner, until perfect fusion is obtained. Fusion takes place in about ten minutes in the muffle, and in about five minutes over the burner. Allow the crucible to cool for a few minutes; then while still warm place in an 800-cc. beaker containing 400 cc. of water. After solution, which takes place quickly, remove the crucible and the cover with iron tongs, and wash them with water from a wash bottle. If excess silica is present, boil before making up to volume. Make up the volume in a graduated flask to 500 cc. and filter the solution through four folded sheets of 8-inch filter paper placed in a 5-inch funnel.

A good grade of bleached paper should be used, because with unbleached paper the organic matter dissolved by the hot caustic solution will require several cc. of permanganate solution for the blank titration. One grade of paper tested was so poor that as much as 10 cc. of one-twentieth normal permanganate was required to colour the filtrate permanently after it had been made acid. The quantity required for blanks in the peroxide fusion method should never exceed 0.8 cc.

Filtration takes place quickly. When 250 cc. have filtered through, stop filtering, add enough dilute (1:1) sulphuric acid to the filtrate so that after the caustic has been neutralised the solution will contain approximately 12.5 cc. of free sulphuric acid. Heat the 250 cc. of acidified solution on the hot plate for several minutes to drive off any hydrogen peroxide that may have formed. The acid solution is then ready to be passed through a Jones reductor.

Interfering Elements.—Fusion with sodium peroxide will completely and readily convert all the molybdenum into soluble sodium molybdate. When the fusion is dissolved in water the iron will be completely precipitated with other insoluble hydroxides, including copper. With low-grade material the amount of molybdenum retained by the bulky precipitate is of no consequence in the calculations. However, with high-grade material, the precipitate should be redissolved and again precipitated, as only an aliquot part of the filtrate is taken for analysis and the amount of molybdenum retained by the precipitate may materially affect the results. Other interfering elements that may occur in the leached molybdenum solution may be removed or determined as in acid decomposition (*ante*).

If the alkaline leached solution obtained by fusing an ore rich in silica is neutralised with dilute acid and an insufficient excess, only a few cc., of acid is present, colloidal silicic acid will be precipitated when the solution is heated. On titrating the solution after it has been passed through the reductor, low results will be obtained, and the end point will fade quickly and be uncertain (see para. "Precaution against Fading End Point," later). The concentration of acid used, 12.5 cc. in 250 cc. volume, prevents this precipitation if the solution is not boiled too long. If too much silicic acid separates, the better plan is to take a new sample rather than attempt to run the gelatinised solution through the reductor.

Jones Reductor.—The Jones reductor is illustrated and described by Lord and Demorest (N. W. Lord, and D. J. Demorest, "Metallurgical Analysis," 1916, pp. 29-30), also by Scott (W. W. Scott, "Standard Methods of Chemical Analysis," 2nd ed., 1917, p. 281). It consists of a glass tube which is contracted at the bottom, with a 3-inch funnel inserted at the top. The internal bore and length of tube are important considerations. The stem of the funnel enters a small one-hole rubber stopper, which fits tightly into the top of a glass tube. The stem, or contracted end of the tube enters the rubber stopper of a 2-litre side-neck flask that is connected by pressure tubing to a suction pump.

The zinc for the reductor should be of 20-mesh size and contain less than 0.01 per cent iron. It is best amalgamated as follows: With very dilute H_2SO_4 —about 3 cc. to 100 cc. of water—moisten in a beaker a sufficient quantity of zinc to fill the reductor, add a small drop of mercury, and stir until uniformly white. Wash the zinc free from acid and put it into the tube. One-half gm. of mercury is sufficient for 150 grms. of zinc. Avoid using more than just enough.

The reductor is filled by placing some glass beads at the neck; on the beads is placed some glass wool mixed with bits of small broken glass rods to prevent the wool from forming a compact plug that might hinder the passage of the solution. Above the wool may be placed a perforated platinum disk or gauze, to assist the clear passage of the solution and to prevent clogging. The tube is then filled to within a few inches of the top with the amalgamated zinc.

The internal bore of the reductor should not be greater than five-eighths of an inch. The reductor should be 20 to 30 inches long. Shorter reductors ranging down to 10 inches, and larger bores than five-eighths of an inch were tried, but the results were unsatisfactory, owing to the following reasons:

(a) The molybdenum solution was not completely reduced by passing the liquid through once, which necessitated passing the solution through a second time, and required a larger blank correction. This factor must be carefully controlled, as shown later.

(b) The quantity of solution or wash water necessary to wash a reductor completely when using one of larger bore than five-eighths of an inch makes the solution too bulky to titrate. In order to obtain a sharp end point the solution must not be too dilute. The titrations obtained on blank runs, with the same quantity of acid and

solution as in a molybdenum determination for several reducers of different construction, varied from 0.5 to 1.5 cc., and, in one test, as high as 2 cc. of 1/20 normal permanganate. The largest blank was later proved to be due to over-amalgamation of the zinc, as the reductor had been used for several hundred determinations and much of the zinc had been dissolved.

Method of Using Reductor.—A stock solution of acid wash water should be made up containing about 50 cc. of concentrated sulphuric acid per litre. 100 cc. of acid wash is passed through the reductor at a temperature of 60° to 70° C., or as hot as can be conveniently handled. This heats the zinc, making the reduction more effective, and removes air from the apparatus. Then the molybdenum solution, heated to the same temperature, is passed through, followed by 200 cc. more of hot acid wash, and 200 to 250 cc. of hot water. The reduced solution should be immediately titrated.

The rate of flow should not be greater than 50 cc. in 30 seconds, and can be accurately controlled by the suction pump. A faster rate may give erratic results, especially with high-grade material.

Care should be taken that no air is drawn through the zinc. If this happens and the air is immediately followed by dilute acid, the liquid running through is sometimes oxidised, possibly from the formation of H_2O_2 ; hence, while the solution and the wash water are being run through the reductor, the surface of the zinc must be kept covered continually with liquid (F. A. Gooch, "Methods of Chemical Analysis," 1912, p. 430). The funnel on the reductor should not be permitted to drain before the run is finished.

Complete reduction is denoted by the green colour imparted to the solution when the molybdenum has been reduced from MoO_3 to Mo_2O_3 . In analysing low-grade material under the given conditions, the use of ferric phosphate solution in the receiving flask of the reductor is not essential, although it is with high-grade ore.

Only enough wash liquid to remove the molybdenum completely should be used. Too much washing increases the blank and makes the titrating solution too large for a sharp end point. After several runs the quantity of wash liquid stated—that is, 200 cc. of hot acid wash followed by 200 to 250 cc. of hot water—was found to wash the molybdenum completely from a reductor ranging from 20 to 30 inches in length and to give a blank determination of 0.35 cc. to 0.50 cc. of one-twentieth normal permanganate solution. This result was as good as could be obtained. Fifty cc. of concentrated sulphuric acid to one litre of water proved to be the best concentration of acid wash. Greater concentration of acid, however, is not detrimental. The concentration of acid in 250 cc. of the molybdenum solution should, as previously stated, be 12.5 cc.

As 1 cc. of one-twentieth normal permanganate solution is equivalent to 0.0016 gm. molybdenum, or 0.16 per cent molybdenum on a 1-gram sample, too much care cannot be taken in the use of the reductor.

Titration.—The determination of the molybdenum in solution will be accurate and dependable only when the following directions for volumetric titration with permanganate are carefully carried

out. The sample of the reduced molybdenum solution that is to be titrated should not be too large, nor the permanganate solution too strong, and before the molybdenum solution is titrated a blank determination should be made exactly as in the molybdenum determination.

Size of Sample.—Five grms. should be taken of any ore supposed to assay less than 3 per cent Mo, 1 gm. of an ore assaying in the vicinity of 15 per cent Mo, and one-half gm. for ore assaying above 15 per cent; a proper aliquot part of the solution should be used when titrating with a weak permanganate solution. The reason for controlling the size of sample is evident. When titrating an aliquot part—for example one-half the weight of the sample taken, as in the method of fusion with sodium peroxide—the reading for one-twentieth normal potassium permanganate should fall on the scale of a 50-cc. burette.

Normality of Potassium Permanganate.—A potassium permanganate solution of approximately one-twentieth normal strength was selected for low-grade material because 1 cc. of such a solution represents 0.0016 gm. Mo., or 0.16 per cent on a 1-gm. basis. A 5-gm. sample of ore containing 0.16 per cent Mo would then require only 5 cc. of the permanganate solution. As the molybdenum content to be determined in low-grade material usually falls below 0.10 per cent, the use of stronger solutions is not advisable because the volume required for titration would be too small for accurate control.

An attempt was made to use a weaker permanganate solution, of 1/100 normal strength, where 1 cc. would represent 0.00032 gm. Mo, or 0.032 per cent on the 1-gm. basis, but the end point of such a weak solution was uncertain and could not be controlled within 1 cc. and often not within several cc. Also a blank determination required several cc. an unreliable quantity. With very high-grade material the use of a solution stronger than 1/20 normal may be necessary in order that a larger sample may be taken for analysis.

Effect of Blank.—When the amount of permanganate required for a blank run is being determined, the acid concentration of the solution, the volume of wash water used, and the manipulation of the reductor should be the same as in the molybdenum determination. One large chemical concern that buys and sells molybdenum ore has not been subtracting a correction factor for ore assaying more than 5 per cent molybdenum, but does subtract the correction for molybdenum content below 5 per cent. The following experiments were made in order to determine the effect of the blank in titrating reduced molybdenum solutions of different strengths. The blank requirement for the reductor used in these experiments was 0.35 cc. of 1/20 normal permanganate.

Two grms. of approximately 100 per cent MoO_3 were dissolved in ammonia and the solution made up to 50 cc. Aliquot portions were drawn off with five different-sized pipettes so that the quantity of molybdenum would correspond to the content found in various grades of ores. The molybdenum in each pipette was carefully determined by the gravimetric method, weighing as lead molybdate, and by titration. Each volumetric determination was made in duplicate or triplicate,

so that the limit of accuracy with this method could also be determined. The results were as follows:

Results of First Set of Experiments.

1. 50 cc. of solution = 0.1327 grm. Mo by gravimetric (PbMoO_4) method.
 50 cc. of solution = 82.60 cc. } 1/20 normal per-
 50 cc. of solution = 82.80 cc. } manganate, volu-
 50 cc. of solution = 82.80 cc. } metric method.
 Average number of cc. required = $82.73 = 0.1324$ grm. Mo.
 Difference from gravimetric = -0.0003 grm. Mo.
 No blank subtraction necessary.

2. 25 cc. of solution = 0.0664 grm. Mo by gravimetric (PbMoO_4) method.
 25 cc. of solution = 41.20 cc. } 1/20 normal per-
 25 cc. of solution = 41.40 cc. } manganate, volu-
 metric method.
 Average number of cc. required = $41.30 = 0.0661$ grm. Mo.
 Difference from gravimetric = -0.0003 grm. Mo.
 No blank subtraction necessary.

3. 10 cc. of solution = 0.0264 grm. Mo by gravimetric (PbMoO_4) method.
 10 cc. of solution = 16.90 cc. } 1/20 normal per-
 10 cc. of solution = 16.90 cc. } manganate, volu-
 metric method.
 Average number of cc. = $16.90 = 0.02705$ grm. Mo.
 $16.90 - 0.35$ cc. (blank subtraction) = 16.55 cc. = 0.0264 grm. Mo.
 Blank subtraction required.

4. 5 cc. of solution = 0.0128 grm. Mo by gravimetric (PbMoO_4) method.
 5 cc. of solution = 8.40 cc. } 1/20 normal per-
 5 cc. of solution = 8.60 cc. } manganate, volu-
 metric method.
 Average number of cc. = $8.50 = 0.01360$ grm. Mo.
 $8.50 - 0.35$ cc. (blank subtraction) = $8.15 = 0.0130$ grm. Mo.
 Difference from gravimetric = $+0.0002$ grm. Mo.
 Blank subtraction required.

5. 1 cc. of solution = 0.002484 grm. Mo by gravimetric (PbMoO_4) method.
 1 cc. of solution = 1.80 cc. } 1/20 normal per-
 1 cc. of solution = 1.90 cc. } manganate, volu-
 metric method.
 Average number of cc. = $1.85 = 0.002960$ grm. Mo.
 1.85 cc. $- 0.35$ cc. (blank subtraction) = 1.50 cc. = 0.00240 grm. Mo.
 Difference from gravimetric = -0.00008 grm. Mo.
 Blank subtraction required.

The results were so significant that the experiment was repeated. A different molybdate solution that had been standardised against pure lead was used, and the molybdenum solution was titrated against lead acetate. In 1 litre of water 4.74 grms. of $(\text{NH}_4)_2\text{Mo}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ was dissolved and standardised against 0.20 grm. of pure lead foil, as given by Low (A. H. Low, "Technical Methods of Ore Analysis," 1913, p. 151), in the determination of lead, using a standard molybdate solution.

Results of Standardisation.

10 cc. of the molybdate solution = 0.0054 grm. Pb = 0.02502 grm. Mo.
 By gravimetric (PbMoO_4) method, 10 cc. of solution = 0.02472 grm. Mo.
 Difference = 0.0003 grm. Mo.
 Average for 10 cc. = 0.02487 grm. Mo.

Results of Second Set of Experiments.

1 cc. of molybdate solution requires 1.90 cc. of permanganate = 0.35 cc. (blank) = 1.55 cc. = 0.002480 grm. Mo.
 5 cc. of molybdate solution requires 7.80 cc. of permanganate = 0.35 cc. (blank) = 7.45 cc. = 0.01202 grm. Mo.
 10 cc. of molybdate solution requires 15.90 cc. of permanganate = 0.35 cc. (blank) = 15.55 cc. = 0.02488 grm. Mo.
 25 cc. of molybdate solution requires 38.60 cc. of permanganate (no blank subtraction) = 38.60 cc. = 0.06176 grm. Mo.
 Difference on 1 cc. = 0.000007 grm. Mo.
 Difference on 5 cc. = 0.0004 grm. Mo.
 Difference on 10 cc. = 0.0001 grm. Mo.
 Difference on 25 cc. = 0.0004 grm. Mo.

These results indicate that no blank should be subtracted on a molybdenum solution that requires more than 16 cc. of a one-twentieth normal permanganate solution; this quantity corresponds to 0.0256 grm. Mo and, on the basis of an 0.5-grm. sample, is equivalent to 5.12 per cent Mo. For a permanganate consumption below 16 cc. a blank should be subtracted. The reason for this conclusion is more evident when one considers the following facts regarding the use of such a weak solution as one-twentieth normal permanganate.

Pure distilled water containing the same acid concentration as used in a determination will usually require 0.20 cc. of one-twentieth normal permanganate to effect a colour in 250 cc.; also, when a blank is run through a reductor, if any H_2O_2 is formed and oxidation takes place in the liquid, some permanganate may be consumed. When a weak solution of molybdenum is run through the reductor, possibly the weak effect of any oxidising substance due to the presence of a trace of H_2O_2 does not act upon the reduced molybdenum; but when a strong solution is run through the reductor an oxidising effect may act upon the reduced molybdenum, and thus compensate for the blank subtraction.

Whether the above explanation is the true one or not, the fact remains that when titrating a strong molybdenum solution no blank need be subtracted. Although the correction may be important when a solution representing an 0.5-grm. sample is titrated, the blank effect is small if the solution represents 2.5 grms. or more. The small blank, 0.35 cc. or 0.50 cc., would then be divided by 2.5 or more in calculating to a 1-grm. basis to obtain the true percentage, and a fraction of one-tenth cc. represents a negligible amount of molybdenum.

(To be continued.)

REMOVAL.—The head offices of Siemens Brothers & Co., Limited and of Siemens Brothers Dynamo Works, Limited, will be removed shortly from Palace Place Mansions, Kensington, London, W.8 to Caxton House, Westminster, London, S.W.1.

REPORT FOR THE YEAR 1919
OF THE
FOOD INVESTIGATION BOARD, DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

(Continued from p. 201.)

Meat Committee.

THE Committee in the past year have concentrated their attention upon the preservation of beef by cold. It is a remarkable fact, familiar to the industry, that whereas mutton can be completely frozen without damage, beef cannot. If it be frozen the colloidal complex in the muscle fibre is altered in such a way as to produce a separation of liquid and solid constituents, so that the meat on thawing drips freely a fluid rich in nutritive material and coloured with hæmoglobin. It is of great importance to the industry to discover a process whereby beef can be frozen as safely and expeditiously as can mutton, and therefore the Cold Storage and Ice Association placed this problem in the forefront of the programme of research which they submitted to the Department.

The result of a year's work is to show that the problem is soluble, at any rate, on the laboratory scale. Beef frozen sufficiently rapidly is indistinguishable, both as to its physical and chemical characters, from fresh beef; it does not "drip" when thawed, and the course of intrinsic chemical change is that of fresh beef and profoundly different from that followed by meat frozen in air.

The investigations have been carried out at the Biochemical Laboratory at Cambridge under the general supervision of Professor, F. G. Hopkins, F.R.S., and in London both at the Physiological Laboratory, University College, and at the Board's temporary experimental station at Leyton, under the general supervision of Professor W. M. Bayliss, F.R.S.

Nitrogenous Autolysis of Beef and Mutton.—

The question whether the difference in the behaviour of beef and mutton when subjected to the process of cold storage could be explained in terms of a biochemical difference in the tissues is obviously at the root of the matter, and Prof. Hopkins decided that this should be the first subject of investigation. The enquiry was entrusted to Mr. W. Fearon and Miss D. M. Foster, and the results obtained show that, whilst beef and mutton do differ in certain chemical qualities, the differences do not provide an explanation of the different physical properties alluded to above. This is encouraging, for though it may be possible to control secondary physical changes it would manifestly be impossible to alter fundamental chemical characters.

Fresh mutton is characteristically more acid than fresh beef and the distribution of nitrogen is different, but the most striking difference lies in the autolysis of the tissues of the two animals. In the case of fresh beef and mutton nitrogenous autolysis, that is to say the intrinsic chemical change which follows on death considered only with reference to the distribution of nitrogen, comes to a stop in seven or eight days at room temperature. The form of the curve of change is, however, different for the two animals, and the

final equilibrium so characteristic as to afford a means of differentiation between the meat of the two species.

These relations, characteristic of fresh meat, are completely upset by the relatively slow freezing which occurs in air at say -10° C. The rate of change is altered and the chemical breakdown much more drastic. Instead of coming to an end in seven or eight days there was no sign of the characteristic equilibrium in sixteen days, the longest period during which the meat was kept under observation.

Experiments on a small scale, that is to say, with pieces of a few pounds in weight, showed that when beef is frozen sufficiently rapidly, e.g., by immersion in brine cooled to -20° C., the characteristic propensity to drip on thawing was eliminated. Attempts were made to reproduce these results on a commercial scale by using quarters of beef, but the plant at the disposal of the workers was not powerful enough to remove the heat sufficiently rapidly. It was noticed in the course of these experiments that immersion in brine led to the natural fresh red colour of the beef deteriorating rapidly when it was thawed. The samples usually appeared a dull and rather dirty purple. The cause of this discoloration was investigated by Miss Foster and found to be due to the conversion of hæmoglobin into methoglobin.

She also found that by careful regulation of the composition of the brine this change did not take place, the beef retaining its natural bright colour. It may be said therefore that the freezing of beef, so that the product on thawing behaves chemically and physically like fresh beef and retains its natural colour is possible. It remains to be seen, however, whether it is feasible as a commercial process. The Board have made arrangements for carrying out the necessary experiments on a commercial scale.

Advantage was taken by Mr. I. Jørgensen and Prof. W. Stiles of the experiments with beef to make a number of observations on the rate of cooling. Thermocouples were placed at different depths in the meat and the temperature recorded electrically. The large number of data so obtained will be published in a general report on the theory of freezing which is now being prepared for the press.

The work on putrefaction has during the year centred on the two points, (1) the conditions which determine the rate of invasion by bacteria and the limits to which they can multiply, and (2) the development of the chemical technique. When a sterile nutrient broth is sown with bacteria there is first of all a characteristic latent period in which growth is practically absent, then a period during which growth is active and the number of bacteria increasing, and a closing period during which the number falls until only a few survivors remain. The number of bacteria per unit volume plotted against time thus follows a characteristic curve. It has been thought hitherto that the cessation of growth and the death of most of the organisms were due mainly to the accumulation of the chemical products of their own activity. In considering the change produced by bacteria in food it is of importance to discover whether this really is so. The experiments of Dr. G. S. Graham-Smith seem to prove that, at least under

experimental conditions and in pure cultures, cessation of growth is due to the using up of some foodstuff which is specific for each of the organisms tried. This follows from the fact that when a nutrient broth which has been exhausted by one species is sown with bacteria of another species the latter grows freely.

The relation of food supply to growth, the influence of the reaction of the medium, the effects of the addition of gelatin and agar to the medium, the influence of previous fermentation in the medium, the influence of the number of bacteria inoculated, the effects of dilution, and the influence of temperature have also been studied. The experiments are now almost completed and the results should be of great service in the study of putrefactive and other changes.

The anaerobic spore-bearing bacilli have been made the subject of special investigation since these undoubtedly play an important part in the process of putrefaction. The study of this important group of bacteria has been hampered by the difficulty in cultivating more than a small proportion of those shown to be present by microscopic methods. Accordingly experiments were made by Mr. F. P. G. de Smidt with a view to the selection of a culture medium in which the survival and growth of a large proportion of these organisms from a given inoculation could be relied upon; and very good results have been secured with a digest broth provisionally called "D₃."

Using pure cultures of 10 different types of anaerobes, it was found that the survival of 80-100 per cent of small seedings of 10-50 bacilli each occurred in D₃ agar without glucose; the same seedings inoculated into ordinary glucose nutrient agar for comparison gave negative or very scanty results.

The preparation of this medium is very simple, cheap and rapid. Accurate adjustment of its reaction is unnecessary for the best results, growth in it is rapid, and no tendency to morphological variation of the bacilli follows its use. The studies in this subject will be ready for publication shortly. Since the results with cultures of known pathogenic and some purely putrefactive anaerobes have been encouraging, it is intended to investigate the distribution of anaerobic bacilli in the various stages of putrefaction, and their relation to the aerobic organisms which are constantly present.

The methods commonly used for estimating the changes occurring in the breakdown of animal matter by the action of enzymes and bacteria have hitherto been so laborious as to render it almost impossible to make observations sufficiently numerous to obtain a knowledge of the rate and order of these changes. Mr. F. W. Foreman therefore set out to devise new methods and he has succeeded in discovering an accurate and simple procedure for estimating the simpler products of bacterial decomposition. (Mr. F. W. Foreman is a Research Officer of the Animal Nutrition Station, Cambridge, and his services were lent for the purpose of this research). Briefly it is as follows:—

The acid radicals of salts of primary, secondary, and tertiary amines, and the carboxyl groups of amino acids can be accurately estimated by titrating their alcoholic solutions if the concentration of alcohol is sufficiently high.

The total acids (including the carboxyl groups

of amino acids), whether in the free state or combined with organic bases, can be quantitatively titrated in alcoholic preparations made from media containing the products of degradation. The removal of the organic bases is unnecessary, and the experiments can be carried out at the ordinary temperatures. Consequently the materials are not subjected to risk of decomposition by heat.

It is proposed to apply this method in investigating:—

- (1) bacterial processes in culture; and
- (2) the order of breakdown of the constituents of meat or fish by organisms in the hope of obtaining clues as to the best means of detecting the early stages of putrefaction so that the quality of such food materials may be gauged.

The systematic and biological investigation of the moulds which infest cold-stored meat have been continued by Mr. F. T. Brooks, assisted by Miss N. Owen, and considerable progress has been made towards a monograph of these fungi. Notwithstanding the fact that the same moulds occur repeatedly a large number of forms have been isolated, some of which are new to science. All these moulds are confined to the superficial layers of the meat, none of them being able to penetrate the tissues deeply.

Special attention has been directed to the "black-spot" contamination of beef and mutton. It is now clear that this trouble is exclusively due to one or more species of *Clad sporium*, a genus of world-wide distribution the members of which grow chiefly upon dead vegetable tissue. It is of interest that the "black-spot" fungus isolated from Argentine beef is identical with that from New Zealand mutton.

Enquiry is being made into the nutritive and physical conditions under which these moulds develop. Although there has been a belief in the trade for some time that certain of them would develop under cold-store conditions, there has always been some doubt as to whether they were not due to some temporary breakdown of the plant during storage either on board ship or elsewhere. It was, therefore, important to perform critical experiments to ascertain whether any of these fungi would develop under uniform cold-store conditions. This has been done, and it has been shown conclusively that the fungus causing "black-spot" will grow and produce spores at a temperature at least 5° C. below freezing point. This fungus develops more readily at low temperatures if, before being placed in the cold, the meat or artificial medium inoculated with the spores is kept for from 24 to 28 hours at ordinary temperature, thus allowing the early stages of germination to take place under normal conditions. Growth is very slow at these low temperatures, but it is greatly enhanced if the temperature is raised to 0° C. So far the "black-spot" fungus is the only one found to grow at a temperature considerably below 0° C., but several others develop fairly well at freezing point. Experiments are being made upon the vitality of spores kept under cold-storage conditions for various periods.

Efforts are being made to ascertain the sources of infection by these moulds, and the New Zealand Government, through the High Commissioner, is kindly helping by giving information in regard to this part of the enquiry.

It is obvious that these lines of investigation must be carried further before suggestions can be made as to the measures to be taken to prevent these mould growths.

Several visits have been paid to commercial cold stores in order to become familiar with the conditions under which the trade operates.

The progress of the work in the experimental cold store is necessarily slow, partly from the nature of the investigation and partly because there is only one small chamber available for this particular inquiry.

Mr. L. F. Newman has completed his trials of the nutritive value of dried blood. This research may be described as part of the war work of the Board rather than as being comprised in its normal activities. At the time of the great shortage of pig foods it was considered advisable to test the effect of the addition of dried blood to such foods as were available. Experiments were carried out at the Animal Nutrition Station, Cambridge, on 28 pigs. What might be called ordinary commercial diets were used to which dried blood was added in amounts varying from 2 ozs. to 6 ozs. per pig per day. The following figures show that pigs fed on a diet to which dried blood was added showed a decided increase in weight above that of pigs on similar diet but without the blood.

Per Seven Days.	Diet	Result after 22 Weeks.
1.	Wheat offals only...	Gained 15st. 7½lbs.
2.	Maize Meal only ...	Lost 3½lbs.
3.	Wheat offal and dried blood ...	Gained 20st. 3½lbs.
4.	Maize Meal and dried blood ...	Gained 14st. 11½lbs.

Also, as remaining over from the war work of the Board, Mr. Newman drew up a careful report upon the Salvage of Slaughter-house Refuse, which has been considered by the Ministry of Food and other Departments.

Engineering Committee.

The work of the Engineering Committee has been carried out by three Sub-Committees dealing respectively with:—

- (1) the general problems of refrigerating agents, of insulation and of hygrometry;
- (2) the design of cars and barges suitable for the carriage of perishable produce; and
- (3) the literature of refrigeration.

To take the last-mentioned Sub-Committee first; it was felt that the work of the Engineering Committee would be furthered if lists of English, American, French, Italian, and German books, journals, and proceedings dealing with refrigeration and cold storage were available for reference. Mr. G. C. Hodsdon and Prof. C. H. Lees, F.R.S., both with special knowledge of the literature of those subjects, were appointed a Sub-Committee. They have completed a bibliography which, though it must be looked upon as the first step in this direction, omits no work of first-class importance. It was thought by the Committee that this bibliography, originally drawn up for its own convenience, might be of value to others interested in the industry. It has therefore been published as Special Report No. 2 of the Food Investigation Board.

The work of the Sub-Committee on Insulation, which is too complex and voluminous to be effectively summarised, and is still in progress, has been carried out mainly at the National Physical Laboratory by Dr. Ezer Griffiths, where special apparatus has been installed in triplicate for determinations of the heat conductivity of materials. Each consists essentially of a relatively warm plate surrounded by a guard ring maintained at the same temperature. The warm plate is fixed symmetrically between two cold plates with the material under test packed in the space between.

The central warm plate consists of two sheets of aluminium, 3ft. by 3ft., while the guard ring is made of steel plates. The temperature of the cold plate is maintained at a constant and determined level by a brine circulation from a refrigerating plant installed for the purpose.

One of the greatest practical difficulties in the past with warm and cold plate methods has been the uneven distribution of temperature over the surface, which has necessitated a troublesome integration to obtain the average temperature. The use of a guard ring and the method devised for the construction of the heating element has overcome this difficulty. By these means uniformity of temperature has been secured over the entire area with very satisfactory results.

It was found that a steady state was not attained until about five days from the time of setting up the temperature difference between the warm and cold plates, consequently the observations extend over many weeks if a series of temperature ranges have to be covered. It is possible that the wide discrepancies in published data are to some extent due to neglect of this precaution. Nearly all the common insulating materials have now been tested through a large range of temperature and this has constituted the main work of the Sub-Committee.

In addition to this principal enquiry investigations have been and are in progress having for their object the elucidation of the laws governing the heat transmission from the walls of the room to the air.

Heat transfer from hot objects is effected by radiation, convection, and conduction. The laws governing the transfer by radiation are well known and it is easy to calculate the magnitude of the effect if the surface emissivity is known, while the transfer by gas conduction is relatively small for most practical cases. The transfer of heat by convection is complicated by the fact that it is dependent on a variety of factors such as the geometrical form of the surface, &c.

As practically nothing is known concerning the laws governing the convection loss in the case of large plane surfaces attention was directed in the first instance to a study of the phenomena as exhibited by a rectangular plate fixed with its surfaces vertical.

When a cold room which is now being prepared becomes available, it is proposed to conduct the experiments on convection at low temperatures, but it is obvious that, within certain limits, the same general laws will apply whatever the absolute temperatures of the surfaces may be.

A complete study of the losses by convection from a plane surface necessitates a knowledge of the temperature, velocity, and stream lines of the

air involved. A determination of these quantities will also afford a valuable check on any theories advanced and so assist in determining the constants associated with any particular wall and temperature.

Experiments were undertaken in which a vertical plate was heated electrically to a steady temperature so that the heat losses were just equal to the heat supplied. In this way the relation between heat loss and temperature was obtained. At the same time measurements of the temperature of the air streams were made, and qualitative ideas on the velocity and direction were obtained by smoke methods. Later, by means of a hot wire anemometer quantitative information was obtained. This instrument is, so far as we are aware, the only type of anemometer that is sufficiently sensitive to measure the low velocities of natural air currents, and in view of the many practical applications which exist for such an instrument and its easy adaptation to measurements of the temperatures of gas streams it was deemed desirable to devote some time to its study.

Radiation losses have been measured, using a thermopile and potentiometer. The method was to point the thermopile at the hot plate, measure the resulting E.M.F. by potentiometer, and then interpose a screen at room temperature and notice the E.M.F. again. The difference gave a measure of the radiation from the hot plate to an enclosure at the temperature of the room. The experiment was repeated with the surface lamp blacked. Thus emissivities were obtained compared with that of lamp black, which was later found to be about 90 per cent of that of an ideal black body. The radiation loss per square centimetre is known to be $e E$, where e is the emissivity and $E = 5.3 \times 10^{-12} (T^4 - T_0^4)$ watts, T being the temperature of the radiating surface and T_0 that of the surroundings.

In this connection special attention was given to the effect of the nature of the surface upon radiation. At any given temperature a black body radiates over ten times as much heat as ordinary polished aluminium. It appeared possible that a certain amount of heat could be saved in insulation by treating surfaces with suitable coverings or paints. One would expect a metallic surface to be better for insulation purposes than ordinary wood, and possibly white enamel would be better covering for wood than dead black paint. Experiments were undertaken to test this. A large cylindrical copper vessel containing hot water was painted in sections with various paints. One section was painted dead black for the standard radiation with which all the others were in the first place compared. The vessel was mounted vertically on a turntable, and a linear thermopile was fixed in position near by. By rotation of the turntable the various sections could be brought in turn before the thermopile. The temperature of the stirred water was not found to alter by more than about 1°C . during a test; it gives approximately the temperature of the radiating surface. Galvanometer readings of the thermopile current were taken (a) with the thermopile pointed at the object, (b) with a screen at room temperature interposed between the thermopile and the object. Deflections are proportional to the radiation from the hot body to the room. The procedure in any experiment was to take the deflection for the standard dead black, to work through the series

of paints, and then to return through the series of paints back to the standard dead black, thus obtaining any progressive change in the thermopile during the series.

Experiments with paints lead to the conclusion that at temperatures below 100°C . all ordinary paints are indistinguishable as regards radiation, but that the metallic paint used shows superiority.

Investigations in hygrometry have been continued at the National Physical Laboratory and at the University of Bristol by Prof. A. M. Tyndall and Mr. H. G. Mayo. Progress has been made, but much remains to be done before the difficulties inherent in hygrometry at low temperatures are overcome.

At Oxford, Prof. C. F. Jenkin has resumed, on behalf of the Committee, his investigations of the physical properties of carbon dioxide and other fluids, in relation to their use as the working substance in refrigerating machines.

The Sub-Committee on Refrigerator Cars and Barges, under Mr. A. R. T. Woods, have continued their experiments on the insulation of railway wagons. It will be remembered that a report on this subject, drawn up by the Sub-Committee has been published by the Board (Special Report, No. 1). During the year trial runs with insulated cars have been made on the Great Western and Midland Railways.

The Sub-Committee began work on insulated barges during 1919 by a series of observations of temperatures on barges actually in use on the Thames. A motor-driven steel barge has been purchased and is now being adapted for experimental work. The hold will be divided into three compartments, the insulation of each of which will be different, so as to permit of simultaneous tests of different insulating materials and methods. An ethyl chloride plant is being installed on board which incidentally will give an opportunity of studying the action of that refrigerant.

Fruit and Vegetable Committee.

Researches have been carried out at the Biochemical and Botanical Laboratories at Cambridge under Dr. F. F. Blackman, F.R.S., at the Imperial College of Science and Technology, South Kensington, under Prof. J. B. Farmer, F.R.S., and Prof. V. H. Blackman, F.R.S., and at the Agricultural and Horticultural Research Station at Long Ashton, which is an outlying station of the University of Bristol, under Prof. B. T. P. Barker.

In order to assist the workers, special chambers for the storage of fruit in which temperature and humidity could be regulated have, by the kindness of the Port of London Authority, been fitted up at one of their cold stores.

A series of storage tests with strawberries at various temperatures, and with various gas mixtures, has been carried out by Dr. Franklin Kidd and Dr. C. West, at the Botany School, Cambridge, as well as a preliminary investigation of the possibilities of preserving this fruit in a frozen or in a dried condition.

It has been found that strawberries, when picked ripe, may be held in cold store (temperature 1° to 2°C .) in a good marketable condition for six to seven days. Unripe strawberries do not ripen normally in cold storage, neither do they ripen when transferred to normal temperatures after a period of cold storage.

World's Production of Monazite—1913 to 1919 inclusive.

	1914	1914	1915	1916	1917	1918	1919
India	1235	1186	1108	1292	1940	2117	2000*
Ceylon	—	—	—	—	—	20	—
Brazil	1415	590	433	—	1118	491	—
United States	—	—	16	17	35	—	—

*Estimated.

World's Production of Chromite in Metric Tons.

	1913	1914	1915	1916	1917	1918	1919
United Kingdom	113	119	—	392	303	—	—
Rhodesia	57,517	43,745	54,974	80,645	66,210	28,390	32,016
Canada	—	—	11,199	24,970	33,326	19,958	7,426
India	5,769	5,984	3,829	20,488	27,503	58,713	—
Australia	688	660	760	621	1,365	730	250
Bosnia and Herzegovina	305	211	370	967	1,805	—	—
Greece	6,342	7,050	10,420	9,880	6,750	10,890	—
Norway	—	81	350	2,757	3,975	—	—
United States	259	601	3,335	47,803	44,439	83,695	3,964
Japan	1,332	2,117	2,991	8,283	8,947	7,244	—
New Caledonia	63,370	71,708	57,474	57,024	41,892	26,000	—

The employment of certain artificial atmospheres in the storage chambers has been found greatly to extend the storage life of strawberries. For example, strawberries when picked ripe can be kept in excellent condition for the market for three to four weeks at 1° to 2° C. is maintained—

- (1) in atmospheres of oxygen, soda-lime being used to absorb the carbon dioxide given off in respiration;
- (2) in atmospheres containing reduced amounts of oxygen and moderate amounts of carbon dioxide obtained by keeping the berries in a closed vessel fitted with an adjustable diffusion leak. Under both these conditions of storage, the growth of parasitic and saprophytic fungi is markedly inhibited, but in each case the calyces of the berries lose their green colour after two weeks.

A method of obtaining strawberries as a dried fruit has been worked out and has yielded good results. The product, which has the appearance of a small reddish fig, and the consistence of raisins or sultanas, retains the strawberry flavour and differs from a fresh strawberry in the same sense as the raisin differs from the grape. The product keeps well, is not attacked by moulds, and is one-quarter to one-fifth the weight of the fresh fruit.

(To be continued).

MINERAL RESOURCES OF THE WORLD.

Monazite.

PAMPHLET issued by the Imperial Resources Bureau, entitled "The Mineral Industry of the British Empire and Foreign Countries."

The production of monazite is limited chiefly to India and Brazil, as shown by the Table which gives the world's production of monazite for the years 1913 to 1919 inclusive.

Monazite owes its commercial value to the presence of thorium oxide, the amount of which varies, best Brazilian containing about 6 per cent and those from Travancore and Ceylon containing about 9 per cent; but it is essentially a phosphate of the cerium earths.

After the extraction of the thorium oxide from monazite, the large amounts of cerium compounds were up to recently useless, but they now supply the cerium required for the manufacture of ferrocerium (containing 30 per cent iron) which is used in the manufacture of sparking devices; also a special variety of optical glass is made into spectacles for use by glass furnace operators to avoid injury to their eyes.

Chrome Ore and Chromium.

PAMPHLET issued by the Imperial Mineral Resources Bureau, entitled "The Mineral Industry of the British Empire and Foreign Countries."

This pamphlet gives statistical and technical information relative to the supply and consumption of chrome ore and chromium during the period 1913 to 1919.

The ore of chromium, known as chromite, chrome ore, chrome iron ore, and chromic iron ore, was for many years mainly mined in Rhodesia and New Caledonia, although small quantities are produced from other countries as shown in the Table, which gives the world's production of chromite in metric tons.

At the present time, chromium has many uses, principally for making the alloy ferrochromium, which is used in the manufacture of armour-plates, rock-crushing machinery, &c. High-speed steels contain from 3 to 5 per cent of chromium. An alloy of chromium with about 75 per cent of iron gives a rustless steel, which is used for the manufacture of cutlery, turbine blades, acid pumps, exhaust valves for aircraft engines, &c.

Stellite is essentially alloy of chromium and cobalt and is used for high-speed cutting tools.

Another important application of chromite is for the manufacture of potassium and sodium chromates and bichromates, which are used in the tanning, dyeing, pigment, and other trades.

A further important use is in the manufacture of chromite bricks for metallurgical use as refractory material for lining furnaces.

The pamphlet gives the relative amounts of chromium ore used for these different purposes as for ferrochrome, 52 per cent of total consumption; for chemicals, 31 per cent of total consumption; for refractories, 17 per cent of total consumption.

NOTES.

MANCHESTER LITERARY & PHILOSOPHICAL SOCIETY.—Professor T. H. Pear, M.A., B.Sc., of the Victoria University of Manchester, has been elected an Honorary Secretary of the Manchester Literary and Philosophical Society in succession to Professor C. A. Edwards, D.Sc.

DISCUSSION ON ELECTROPLATING.—A joint meeting organised by the Faraday Society and the Sheffield Section of the Institute of Metals will be held in the Mappin Hall of the Department of Applied Science of the University of Sheffield, St. George's Square, on Friday, November 19, to discuss papers dealing with various aspects of electroplating. Communications are promised from representatives of the scientific side of the Electroplating industry in London, Birmingham, and Sheffield. Those desirous of taking part are invited to communicate with the Sheffield Local Honorary Secretary of the Faraday Society, Dr. F. C. Thompson, Department of Applied Science, University of Sheffield.

WILDE-BARFIELD ELECTRIC FURNACES.—Messrs. Cross, Son, & Robertshaw have been appointed sole selling agents for the counties of Northumberland, Durham, Cumberland, and Yorkshire. In addition to their office in Newcastle, Messrs. Cross, Son, & Robertshaw have opened a branch office at 41, Great George Street, Leeds, where a Demonstration Furnace is in course of erection. Messrs. Macbeth Bros. & Co., Ltd., of Bombay and Calcutta have taken over the sole selling rights for India, where these plants are already in operation.

THE Association of British Chemical Manufacturers have recently issued a list of "Research Chemicals" which has been compiled at the request of the Chemical Society and the Institute of Chemistry. The list is very complete and speaks well for the enterprise of the Manufacturers concerned. The manufacture of fine chemicals is now recognised as a key industry and is of vital importance to the welfare of the Empire in times of war, and must therefore be fostered and encouraged in times of peace. The next few years will be critical in the establishment of the industry on a permanent and successful basis, and unless it receives sympathetic treatment by the Government and support from Research Chemists and the general public, it will inevitably fall back into its pre-war state of comparative insignificance. The chemicals mentioned in this pamphlet are made and/or supplied by British firms as indicated. There are certain chemicals in the list, a permanent supply of which cannot be guaranteed unless there is sufficient demand. All the distributing houses are in possession of this list and the manufacturers prefer that orders should be sent through the usual trade channels. In special cases, of course, applications may be sent direct to the manufacturers when they will be dealt with according to the custom of the firm concerned. This list must be regarded only as a preliminary one which, it is hoped, will be supplemented considerably from time to time. The manufacture of new chemicals will be undertaken by one or other of the firms according to demand. All questions of difficulty and enquiries

for chemicals not in the list should be referred to the Association of British Chemical Manufacturers, 166, Piccadilly, W.1., when every endeavour will be made to meet the requirements of Research Chemists.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

L'Age de Fer, No. 1606

THE MINERAL WEALTH OF EASTERN SIBERIA.—The article gives a brief account of the minerals that can be found in Oriental Siberia, and says that, according to surveys made, the provinces of Anadyr and Amour, in spite of their distance away, are destined to a great future prosperity. Metallic gold is found in the sandy loam, notably in Haut-Amour and in the Anadyr basin. The thickness of the alluvial deposits vary from three to six metres, except in the Niman region where it attains a thickness of 20 metres.

The following figures are given for the production in 1915:—

	Kilograms
From the Amour district	907
" Bureya district	1545
" Leya district	1123
" Maritime district	2297
" Oussouri district	72
	6034

Iron abounds in the form of magnetite and haematite. The annual output up to the present is approximately 18,000 tons. The Japanese and Americans are the principal users of these ores.

Silver, Lead, and Zinc.—Sulphide ores, galena, and blende, also calamine, smithsonite, are found in quantity. The best known veins are those which stretch from the Chankotsk peninsula up to Korea, especially in the Tsetioukhe region. These veins are estimated to be able to yield nearly 2,000,000 tons of ore, containing 12 per cent lead, 17 per cent zinc, with 280 grms. of silver per metric ton.

Copper.—There are numerous indications of the presence of copper ores, but up to the present only two veins in the Oussouri district have been worked.

Antimony.—Considerable veins of antimony have been discovered in the Bogouchan Mountains.

Coal.—The coal veins of Oriental Siberia, all more or less exist on the Pacific Coast. They are promised an important future. They comprise many different qualities of coal, from lignite to anthracite. Except in the Kamtchatka region and north of this, most of the bituminous coal is of jurassic age. The carboniferous beds of Sakhalin Island and of the Kamtchatka Peninsula are analogous to the deposits found in Japan, Canada and Alaska. Sakhalin Island contains the richest deposits and of the best quality in Oriental Siberia. The deposits of Siberia are estimated at more than 3 milliards of tons.

Petrol.—Soundings for oil on Sakhalin Island have been made since 1908, which has led to the discovery of a large petroliferous field.

MEETINGS FOR THE WEEK.

Monday, November 1.

Royal Institution, 5. General Meeting.

Wednesday, November 3

Society of Public Analysts, 8. "Gravimetric Estimation of Bismuth as Phosphate and its Applications in Ore Analysis" by W. R. Schoeller, Ph.D., and E. F. Waterhouse.
 "Time Factor in Saponification" by Percival J. Fryer, F.I.C.
 "Position of Analytical Chemistry in France" by Victor Cofman, B.Sc.
 "Apparatus for collecting samples of water at great depths" by W. T. Burgess, F.I.C.

Thursday, November 4.

Royal Society. "Vibrations of an Elastic Plate in Contact with Water" by Prof. H. Lamb.
 "Transmission of Electric Waves around the Earth's Surface" by Prof. H. M. Macdonald.
 "A Re-examination of the Light scattered by Gases in respect of polarization." II. "Experiments on Helium and Argon" by Lord Rayleigh.
 "Dilatation and Compressibility of Liquid Carbonic Acid" by Prof. C. F. Jenkin.
 "Radiation in Explosions of Hydrogen and Air" by W. T. David.
 "Photochemical Investigations of the Photographic Plate" by R. E. Slade, D.Sc., and G. I. Higson.
 "Relationship between Pressure and Temperature at the same Level in the free Atmosphere" by E. H. Chapman, D.Sc.
 "Note on Vacuum Grating Spectroscopy" by Prof. J. C. McLennan, F.R.S.

Chemical Society, 8. "The Preparation of 4-, 5- and 6-methylcoumaran-2-ones, and some derivatives of O-, m- and p-toloxylacetic acids" by L. Higginbotham and H. Stephen.
 "A New Method for the Preparation of 2:4-dihydroxy- and 2:4:4-trihydroxy-benzophenone, and some Observations Relating to the Hoesch Reaction" by H. Stephen.
 "Triphenylarsine and Diphenylarsenious Salts" by W. J. Pope and E. E. Turner.
 "The Preparation and Physical Properties of Carbonyl Chloride" by R. H. Atkinson, C. T. Heycock and W. J. Pope.
 "Interaction of Ethylene and Selenium Monochloride" by H. W. Bauser, C. S. Gibson and W. J. Pope.
 "A Study of the Reactions of Sugars and Polyatomic Alcohols in Boric Acid and Borate Solutions with some Analytical Applications" by G. Van B. Gilmour.
 "The Sulphonation of Glyoxalines" by F. L. Pyman and L. A. Ravald.
 "O- and p-toluenesulfoxalines" by F. L. Pyman and L. A. Ravald.
 "Investigation of Sodium Oleate Solutions in the Three Physical States of Curd, Gel and Sol" by M. E. Laing and I. W. McBain.
 "The Constitution of Polysaccharides." Part I. "The Relationship of Inulin to Fructose" by J. C. Irvine and E. S. Steele.
 "The Preparation of Ethyl Iodide" by B. E. Hunt.
 "Action of Sulphur Trioxide on Aromatic Ethers" by R. C. Menzies.
 "Researches on Residual Affinity and Co-ordination." Part II. "Acetylacetones of Selenium and Tellurium" by G. T. Morgan and H. D. K. Drew.
 "The Formation of 2:3:6-Trinitrotoluene in the Nitration of Toluene" by R. B. Drew.
 "The Formation and Reactions of Imino compounds." Part XX. "The Condensation of Aldehydes with Cyanoacetamide" by J. N. E. Day and J. F. Thorpe.
 "The Formation and Stability of Spiro-Compounds." Part III. "Spiro-Compounds from Cyclopentane" by O. Becker and J. F. Thorpe.
 "Condensation of Dimethyldihydroresorcin with Aromatic Aldehydes" by H. Chattopadhyaya and P. C. Ghosh.
 "The Influence of Lead on the Catalytic Activity of Platinum" by E. B. Maxted.

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 3062, December 6th, 1918.
 3063, December 20th, 1918.
 3064, January 3rd, 1919.
 3066, January 17th, 1919.
 3068, January 31st, 1919.
 3069, February 7th, 1919.
 3070, February 14th, 1919.
 3075, March 21st, 1919.

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NOTICES.

EDITORIAL.—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the Editor.

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T. J. REES, B.A.,
Director of Education,
Education Offices,
Swansea.

11th October, 1920.

THE Council of The Linen Industry Research Association are desirous of appointing a Senior Research Physicist and an Assistant Research Physicist to conduct work of a physico-chemical and physical nature in connection with the Linen Industry. According to qualification for the position the remuneration offered will be about £700 and £400 respectively. Application Forms may be had on application to the SECRETARY, Research Institute, Lambeg, Belfast.

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THE CHEMICAL NEWS.

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EDITORIAL.

THE Joint Meeting of the Faraday Society and the Physical Society that was held at the Hall of the Institution of Mechanical Engineers on Monday, October 25, adds one more to the important series of joint meetings that have recently been arranged by the Faraday Society under the Presidency of Sir Robert Hadfield. The subject, "The Physics and Chemistry of Colloids," is one of the greatest importance at the present time; the bearing upon manufactures, and indeed upon every sphere of industry of those bodies whose dimensions lie between that of the molecule and the smallest macroscopic particle, is only beginning to be realised.

The Science of Colloids, although dating from the time of Graham, is still in its infancy, but judging from the volume of the papers that were read at the meeting and from the enthusiasm shown by the speakers, that "infancy" is a very vigorous one.

We understand that the complete "Discussion" will be published before long, but the "Introduction," by Professor Dr. The Svedberg, of the University of Upsala, is of such interest that we are reproducing it at once and hope to publish others of the papers as space may permit.

THE PHYSICS AND CHEMISTRY OF COLLOIDS AND THEIR BEARING ON INDUSTRIAL QUESTIONS.

A SHORT SURVEY OF THE PHYSICS AND CHEMISTRY OF COLLOIDS.

By DR. THE SVEDBERG, Professor of Physical Chemistry, University of Upsala.

THE science of colloids is a science of the micro-structure of matter. In it is reflected the tendency of modern natural science to deal more and more intensely with problem of structure in its full extent. In the great science of the structure of matter, the science of colloids forms the domain that lies above molecular dimensions and beneath macroscopic dimensions. In this domain we have a great number of those systems which are the basis of our material culture and the basis of life as a whole. All living beings are built up of colloids; almost all our food, our articles of clothing, our building materials, are colloids. Or, to mention some special systems, protoplasm, proteins, glue, starch, all kinds of fibres, wood, brick, mortar, cement, certain kinds of glass, rubber, celluloid, &c. The importance of colloid science for many industrial questions is, therefore, beyond all doubt.

The science of colloids is a rather young one. The field of study which it concerns has for a long time been disregarded. In order to be able to treat with success all the questions presented to us by industry, there is still much to be carried out in the department of pure colloid science. In what follows, I will try to give a short review of

the scientific results so far obtained and of the problems which, in my opinion, need especial attention.

The various branches of colloid science are connected to such an extent that it is very difficult to treat the different questions separately. We will try to fix our attention on two principal problems: (1) the *formation of colloids*, and (2) the *changes of structure* in colloid systems. Connected with both these is the problem of the *properties of colloids* and the changes in these properties during the processes mentioned under (2).

The formation of a colloid may be effected in two ways, different in principle, viz., by *condensation* and by *dispersion*, according as one tries to obtain a microstructural system, a colloid, from a molecular structural or a macrostructural system.

In the case of a condensation process, the degree of "graininess" or the degree of dispersion will become higher as the degree of supersaturation increases; which must, of course, always precede condensation. This is the case when fogs are formed by adiabatic expansion of gases. *e.g.*, cloud-formation in the atmosphere, when metal colloids are prepared by condensation of metal gas from the electric arc, when a slightly soluble substance, *e.g.*, barium sulphate, is precipitated by means of a reaction between ions. The condensation always proceeds from certain heterogeneities in the medium; condensation centres or nuclei. As such nuclei, we may have particles of the substance which is to be formed by the condensation, *e.g.*, precipitation of gold on small gold particles when preparing gold hydrosols or gold ruby glass, or gas ions, *e.g.*, fog formation in gases at low degrees of supersaturation, or complex molecules, *e.g.* fog-formation in gases at high degrees of supersaturation. The manner in which these nuclei are introduced into the system under condensation is of great importance for the degree of dispersion of the colloid resultant. If the nuclei are not introduced into the system all at once, but gradually in the course of the condensation process, the particles will be very unequal in size.

The biologically important colloids, *e.g.*, the proteins, are evidently all formed by condensation, but no details of this process are known. The tendency towards condensation manifests itself in the fact that even the protein molecules are, from a purely chemical point of view, condensation products.

In case of a dispersion process, there is always work to be performed against the surface tension or the cohesion force. Accordingly, such a process is, in contradistinction to a condensation process, a forced and not a spontaneous one. We know very little as to the relation between degree of dispersion and experimental conditions. When emulsifying fats and hydrocarbons, the surface tension may be lowered by the addition of small quantities of alkalies or soaps. Grinding, in general, does not lead to a very high degree of sub-division; but it is possible to increase the latter by adding an indifferent solid diluent which can easily be dissolved and removed, leaving the disperse phase suspended in the solvent used. Thus, colloid sulphur has been prepared by grinding sulphur with urea and putting the substance in water. A combination of grinding and

chemical effects on the material may also be used. It seems that, in many cases, a prevention of the aggregation of the particles by means of suitable additions ought to render possible the preparation of high disperse systems by pure grinding. Bubbles and foam might be regarded as a kind of colloids formed by dispersion. On spontaneously breaking up, they form new disperse systems in which the phase that was previously the continuous one becomes the non-continuous one, and *vice versa*. The system: "soap foam—air," with the soap solution as the continuous and the air as the non-continuous phase, is transferred, on account of surface reduction, *i.e.* condensation, into the system: "soap solution drops—air," with the air as the continuous phase. Mercury foam in water (produced by means of pressing water through mercury) breaks up into a mercury hydrosol partly very fine-grained.

A newly-formed colloid may, immediately after its formation, undergo changes of structure of a more or less profound nature. On the other hand, it is nearly always possible to prevent the occurrence of such changes, and therefore we have a right to distinguish and investigate the *primary* structure as the direct result of the colloid-forming process. Colloids with primary structure may conveniently be called *primary colloids*.

We have at our disposal several methods for the closer study of the structure. Almost every property of a colloid depends on the structure, and therefore, conversely, from the study of the properties of colloids we may draw conclusions as to their structure.

The most important and most obvious means is the microscope and the ultramicroscope. With their aid, it is often possible to settle whether the colloid under investigation is of a grainy structure, *e.g.* a colloid gold solution in water, a gold hydrosol, or of a foamy structure, *e.g.* high disperse soap foam, or of a fibrous structure, *e.g.* soap solutions of a certain concentrations. The number and approximate size of the discontinuities, *e.g.* the particles, may also be determined in this way. One may, for instance, count in the ultramicroscope the number of particles observed in a certain volume of gold hydrosol, and by means of analysis determine the content of gold present in the sol. From these figures we get the mass and approximate size if, for instance, we make the assumption that they are spherical. On the other hand, the ultramicroscope gives little or no information about the form or structure of the particles.

A means of deciding whether the particles are symmetrical is to be found in the study of the behaviour of the colloids in magnetic or electric fields. Non-symmetrical particles are oriented by such fields and thereby impart to the colloid a certain, though in general very slight, degree of double refraction, which may easily be measured with great accuracy. In this way, we have been able to settle that the particles in common sulphur hydrosols, prepared by oxidation of hydrogen sulphide, are spherical; but sulphur hydrosols, prepared by grinding sulphur with urea, are dissymmetrical. The particles in gold hydrosols prepared by reduction are dissymmetrical to a high degree.

Two other optical properties, *viz.*, the light absorption and its accompanying phenomena, the scattering and polarisation of light—the Tyndall

phenomenon—may also in certain cases be used for structure studies. Theory, as well as practice, proves that these phenomena are, for instance, dependent to a great extent on the degree of dispersion of the sol. The form and structure of the particles also influence the said properties, but in a manner hitherto unknown. The emission of light from illuminated particles especially—the Tyndall light cone—varies to a great extent with the size of the particles or the degree of dispersion. Colloid solutions that contain very small particles, *e.g.* Faraday's gold hydrosols, give only a slight emission; the light one is scarcely visible. Those with large particles, *e.g.* gold sols made from Faraday's gold sols by allowing the particles to grow in a reduction mixture, emit very much light; the Tyndall cone is very prominent. The optical properties of the particles also play a great part. Thus metal particles emit much light, particles of silicic acid or gelatin only a little.

The resistance exerted on the particles by the surrounding medium when they move under the influence of a force is a means of investigation that is now often used for the determination of the size of the particles. In some cases, *e.g.* when a sol is filtered through a membrane of collodium or gelatin (ultrafiltration), the connection between the resistance and the size of the particles is not known in detail, but we are justified in assuming that the resistance rises with the size of particles. The small particles are more rapidly pressed through the filter than the large ones. Certain kinds of filters transmit molecularly dissolved substances, but not colloids; an important method of separation, especially in biochemistry. If a colloid is separated from a great quantity of dispersion medium by such a membrane, the molecularly dissolved substances—the crystalloids—diffuse through the membrane, leaving a colloid of a purer state—Graham's dialysis. If the particles are spherical and move through a liquid, the resistance is $6\pi\eta r v$, where η is the viscosity, r the radius, and v the velocity. If the force that causes the movement is known, *e.g.*, gravity, the radius may be calculated.

Thus, by measuring the velocity of sedimentation, the radius can be found.

We have

$$r = \sqrt{\frac{9\eta v}{2(s_1 - s_2)g}}$$

where s_1 is the specific gravity of the particle, s_2 that of the liquid, and g the gravity constant.

Even when no exterior forces are acting, the particles in a colloid solution are in movement because of the impacts from the surrounding molecules. This is the so-called Brownian movement, which has attracted so much attention of late. According to the kinetic theory of the Brownian movement, which has been fully confirmed experimentally, each particle, whatever its size and nature, has the same translatory energy as a molecule, *i.e.* $\frac{3RT}{2N}$, where R is the gas constant,

T the absolute temperature, and N the Avogadro constant. Because of the resistance of the surrounding medium, the mean value of the quadratic of the distance traversed in the time t by the particle is $2Dt$, where D , the diffusion constant

of the particles, has the value $\frac{RT}{N} \cdot \frac{1}{6\pi\eta r}$. Thus, if the displacement of the particle is measured the radius must be found. In certain cases it is more convenient to measure D directly and then calculate r by means of this experimental value.

Owing to the fact that the size of the particles is rather great in comparison with that of the molecules, colloids diffuse very slowly compared with crystalloids. As a matter of fact, Graham the founder of colloid chemistry, regarded this property as the fundamental difference between colloids and crystalloids. We know now that between colloids and crystalloids—so very different in their extremes—there exist all degrees of transition forms, and therefore all degrees of diffusibility.

The size of particles may also be determined by measuring the sedimentation equilibrium, *i.e.* the distribution of the number of particles per cc. under the joint influence of gravity and the Brownian movement. In this equilibrium, the concentration of the colloid diminishes exponentially with increasing height, as is the case with the atmosphere surrounding the earth.

We have

$$n_2 = n_1 \cdot e^{-\frac{RT}{N} \cdot \frac{4}{3}\pi r^2 (s_2 - s_1) g (x_2 - x_1)}$$

where n_1 is the number of particles at the height x_1 , n_2 that at the height x_2 .

Hence

$$r = \sqrt{\frac{RT}{N} \cdot \frac{\ln \frac{n_1}{n_2}}{\frac{4}{3}\pi (s_2 - s_1) g (x_2 - x_1)}}$$

The osmotic pressure of a colloid solution is determined; as far as the colloid in it is concerned, only by the number of particles per cc. (n).

We have

$$p = \frac{RT}{N} \cdot n.$$

Consequently, the osmotic pressure is a measure of the degree of dispersion. The osmotic pressure of a colloid is often determined by means of a common osmometer, provided with a membrane permeable to crystalloids, but impermeable to the colloid particles. Now, however, owing to ion adsorption, the particles are, in most cases, surrounded by an electric double-layer of ions, and the colloid thus acts as an electrolyte, one ion of which is able to penetrate the membrane, but not the other. This causes complications. A so-called membrane equilibrium is formed, and the osmotic pressure found is not a real measure of the structure of the colloid.

Owing to the Brownian movement, the number of particles in every small volume of a sol undergoes spontaneous and incessant fluctuations. Hence the value of every property of the colloid in the small volume fluctuates.

We have

$$n = \frac{e}{v} \cdot \frac{n}{n}$$

where n is the momentary value of the number of particles in the small volume v and \bar{n} the mean value.

This phenomenon, predicted by the kinetic theory for colloidal as well as for molecular solutions has been the subject of extensive investigations. The results are of importance because they show that Boyle's law holds good very exactly for dilute colloid solutions, and because of the light they have thrown on the applicability of the probability calculus to a natural phenomenon. From these studies we have also obtained a deeper comprehension of the conception of entropy. For they have shown, in a direct and experimental way, that the law of the incessant growth of entropy only holds for macroscopic systems.

It often occurs that the particles of a colloid are so small to be measured directly, *e.g.* by means of the ultramicroscope or by determining the velocity of sedimentation. In some of these cases one can overcome the difficulty by depositing gold on the particles, thus increasing their size. This method has already been applied to sols of almost all the metals and to sols of some sulphides. If the quantity of gold in a particle is known, it is easy to calculate the radius in the usual manner.

In most colloid solutions and precipitates there are particles of various sizes, and the investigator should, of course, be able to determine not only the mean size, but also the real structure of the sol, *e.g.* the law governing the distribution of the various sizes of particles. Among the phenomena reviewed above only the velocity of sedimentation, the sedimentation equilibrium, and the Brownian movement have been used in studying the distribution of the size of the particles. On the basis of the former phenomenon just mentioned a method has been worked out which has already provided us with much valuable information as to the formation of the various particles in colloids and the agglomeration processes taking place in them.

(To be continued.)

THE CONSTITUTION AND STRUCTURE OF THE CHEMICAL ELEMENTS

THE FIFTH PRINCIPLE (continued).

By HAWKSWORTH COLLINS.

SINCE it has been proved that it is not a matter of chance that in 26 cases out of 44, an element has been found to exist in its ultimate matrix in association with simpler elements, the sum of whose atomic weights is equal to the atomic weight of that element, and whose valences explain the valency of that element; and since it has been shown that in many cases the particular integer obtained as the atomic weight of an element is not only especially suitable for explaining the properties of the element in comparison with the two adjacent integers, but also that frequently it is especially suitable in comparison with several adjacent integers; and since it has been shown that chemists admit the possibility of large errors in the atomic weights; and since also it has been proved that there are large errors; it is evident that some may be expected in the integers obtained from the experimental atomic weights, and that these errors may be corrected by observing the special suitability of adjacent integers.

Thallium (204) = Cu, Se.

The mineral crookesite is Cu₂Se, Tl₂Se, Ag₂Se. Thallium is widely diffused in Fe, Cu pyrites.

Berzelianite = Cu_2Se with Ag, Tl, Fe.

There is evidently only one possible combination of elements, viz., Cu_2Se , which can be said to be especially associated with Tl; and it happens that its molecular weight is exactly equal to the experimental atomic weight of Tl, when $O=16$. The probability that the weight of the only associated combination of elements would accidentally happen to be 204 is something like 1:100. Tl will probably be found later to be a tetrad although at present it seems to be recognised only either as a monad or a triad, for Cu_2Se must form an artiad to be in accordance with the theory.

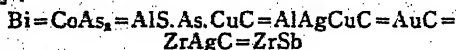
Bismuth (209) = $\text{CoAs}_2 = \text{AuC} = \text{ZrSb}$.

Native bismuth is abundant and intimately mixed with CoAs_2 , especially in Saxony.

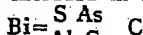
Bismutite is found with auriferous quartz in the Transvaal. Bismuthinite, a sulphide of bismuth, occurs with gold in Rowan Co., N.C. Bismite, an oxide of Bi, occurs with native gold at Berezov in Siberia. Bismuth-gold, Au_2Bi is found in quartz at Maldon, Victoria. •

Bismuth is also found with Sb in kobellite, hauchecornite, and chiviatite; and as Zr is especially found with Au it must also be found with Bi.

These mineralogical facts suggest the three combinations, each of which has a weight of 209, and which are connected with one another by the interrelationship of the elements in the following way:—



and they are all included in the formula:—



where $\text{AlCu} = \text{Zr}$, $\text{AlS} = \text{Co}$, $\text{SAs} = \text{Ag}$, $\text{CuC} = \text{As}$, $\text{AgC} = \text{Sb}$.

Whilst the number 209 is exceedingly suitable, 207 is extremely unsuitable for explaining scientific facts with regard to Bi. Each of the pairs HPb, OsO, NaW, TeBr, SrSb, YSr, RuPd, make up a total weight of 207, but not one of them can be said to be connected with Bi. Also 207 equals 9×23 , but the non-metallic nature of Bi could not be explained by this combination.

Since it has been proved that the actual atomic weight of an element is distinguished by its ability to co-ordinate mineralogical and chemical facts, it is clear that the evidence in favour of the number 209 is very great indeed. The experimental percentage error involved is not as great as that which is suspected by the International Committee in the cases of Zr and B.

The six elements Cu, As, Ag, Sb, Au, Bi, all of which are concerned in the above matter, are connected in the Periodic Table in the following manner:—

Column of monads.	Column of pentads.	C
Cu 63	As 75	75 = 63 + 12
Ag 107	Sb 119	119 = 107 + 12
Au 197	Bi 209	209 = 197 + 12

so that a difference of 12 in the atomic weight in each case corresponds to a difference of four valences.

Zinc (65) = KCN.

The evidence of mineralogy is that the ultimate matrix of Zn is a zinciferous clay, which occurs at Friedensville (e.g.) in considerable abundance

with calamine, an oxide of Zn and Si. Seamon (Dana) says that the calamine has been gradually crystallised out of the zinciferous clays, *these having been first formed*.

Zinc is found in the ashes of the yellow pansy growing in Rhenish Prussia in soil which contains Zn. The power of vegetable life has probably atomised the KCN in the plant and thus produced in the soil a deposit of Zn, the accumulation of ages.

Zn and KCN are both employed for dissolving silver, and their properties are similar in several other ways.

The integer 65 is nearer than 66 to the experimental atomic weight.

Cadmium (111) = Na_2Zn .

Cd is found in smithsonite (ZnCO_3). Greenockite (CdS) is found as a coating on sphalerite (ZnS).

Zn and Cd are the only elements, besides N, which according to this theory are exceptions to the Odd and Even Rule, the reason being that they contain N.

Caesium (131) = Na_2K .

This element is found with Rb (Na_2K), K and Na in rhodizite.

There is no combination of associated elements which is at all suitable for explaining the properties of Cs when 133 is taken as its atomic weight, but the above formula for the atomic weight 131 is exactly suitable in all respects, for it explains why Cs is similar to Rb and K, why it is generally a monad and sometimes a pentad as in CsI_5 , also why it cannot act as a non-metal, and it is in beautiful conformity with the mineralogical facts and also with the large generalisation with regard to Na.

In addition to all this the number 131 is confirmed as the atomic weight of Cs by the following independent investigation, which is only a small part of a very extensive and exact discovery of which a considerable portion has been sent to the Nobel Institute of Sweden. In the following Table, the first column gives the formula of the atom or molecule, the second column gives the relative volumes, the third the difference between the relative volumes of K and Na, the fourth the calculated S.G., the fifth the observed S.G., and the sixth gives the names of those scientists who obtained the exact, or, who were the nearest to the calculated S.G. The relative volumes are in every case calculated from specific gravities obtained at 15°C . or reduced to 15°C .

It is evident from the Table that atoms of K and Na in combination occupy exactly half the volume that they occupy respectively when uncombined. Therefore the volume of an atom of K in combination in the above eight molecules is $44.58/2 = 22.29$; and the volume of an atom of Na in combination is $23.7/2 = 11.85$.

The S.G. of Cs is given as:—

1.872	} 15°C . by Setterburg in Clarke's Table of S.G.'s.
1.884	
1.886	

The mean of these three values is 1.88.

If 131 (= $4 \times 23 + 39$) be taken as the atomic weight of Cs instead of 133, and if the former number be divided by 1.88, 69.69 is obtained as the relative volume of an atom of Cs.

Formula.	Rel. vol.	Diff.	Calc. S.G.	Obs. S.G.	Observer.
K	44.58		0.875	0.8750 13°	Baumhauer
Na	23.70	20.88	0.97	0.97223 15°	Gay Lussac
				0.97	Troost
				0.9686 16.9	Hagen
K ₂ F ₂	55.24		2.099	2.096 21.5°	Clarke
Na ₂ F ₂	34.36	20.88	2.45	2.558 14.5°	Clarke
K ₂ Cl ₂	74.75		1.98	1.98 22°	Spring
Na ₂ Cl ₂	53.87	20.88	2.153	2.153	Schroder
				2.155 15.5°	Holker
K ₂ Br ₂	90.77		2.60	2.672	Playfair
Na ₂ Br ₂	69.89	20.88	2.92	2.505 18°	Spring
				2.704 18°	Spring
				2.952	Schiff
				2.448	Quincke
2KIO ₃	113.47		3.77	3.802 18°	Clarke
2NaIO ₃	92.59	20.88	4.277	4.277 17.5	Kremers
2KNO ₃	95.86		2.10	2.100	Schiff
2NaNO ₃	74.98	20.88	2.266	2.265	Buignet
K ₂ CO ₃	65.05		2.12	2.105	W. C. Smith
Na ₂ CO ₃	44.17	20.88	2.40	2.267	Filhol
2KHCO ₃	97.05		2.061	2.407 20.5°	Favre
2NaHCO ₃	76.17	20.88	2.208	2.078	W. C. Smith
				2.012	Gmelin
				2.207	Schroder
				2.2208 15°	Stolba

The relative volumes of Na and K have been shown to be 11.85 and 22.29, and $4 \times 11.85 + 22.29 = 69.69$.

If any value but 131 be taken for the atomic weight of Cs, this exact correspondence could not take place.

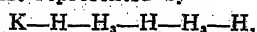
In order to lead up to the constitution and structure of the radio-active and certain other elements, it is necessary first of all to consider the two elements Ti and Cr more fully than in previous papers.

Titanium (48) = K—H—H₂—H—H₂—H and Mg₂.

Titanium is especially associated with minerals which contain much Mg, such as chrysolite, pyroxene, serpentine, amphibole, and phlogopite.

Titanite is an oxide of Ca, Ti, Si.

There are three crystalline minerals, all of the same composition (TiO₂) viz., rutile, brookite, and octahedrite. Of course, there are other cases of trimorphism known, but this peculiarity with regard to Ti seems to be much more marked than in other elements, at any rate in mineralogy. If two atoms of Mg were to become atomised, they could form a metallic tetrad represented either by NaHNaH or HNaNaH, but they could not form the non-metallic hexadic atom which is known to exist represented by



and which could only be formed by the union of an atom of Ca with two of helium. The latter is the only form of the three which could produce titanic acid; so that if it were found that titanium cannot always produce titanic acid, an experimental corroboration of these deductions would be obtained.

Chromium (52) = MgSi.

Chromite, an oxide of Fe and Cr, is found in large masses in serpentine, which is an oxide of Mg and Si.

In addition to the sum of the atomic weights of Mg and Si being 52, the union of the dyad Mg with the non-metallic tetrad Si could produce the non-metallic hexad Cr.

Palladium (104) = Cr₂ = Mg₂Si₂ = TiFe.

Pd is always found with Ir, Os, Pt, Au, Cu, and chromite in the R. Pinto, Columbia, S. America. It is always associated with Pt which is found in Nishni Tagilsk with chromite in a serpentine probably derived from a peridotite; also in the sand of the R. Ivalo, N. Lapland, probably derived from a serpentine (altered peridotite) containing chromite and diallage (pyroxene); also from R. Tayaka, New Zealand, from a region characterised by a chrysolite rock (dunyte) with serpentine. Ilmenite, an oxide of Fe, Ti, is found in serpentine.

The number 106 is entirely unsuitable, whilst 104 is exactly suitable in every respect. Probably the impossibility of completely separating Pt from Pd causes the experimental atomic weight to be higher than it ought to be.

Platinum (194) = ZrPd.

Pt is especially found with Pd in auriferous sands, and crystals of zircon are very common in such sands.

There are now four reasons why the atomic weight of Pd may be expected to be 104 instead of 106 :-

Associated elements found in the matrix of Pd and Pt	Cr ₂	104
	Mg ₂ Si ₂	104
	TiFe	104
	PdZr	104 + 90

Lanthanum (138) = $ZrTi$. *Cerium* (140) = Na_2Ti .

La, Ce, Zr, and Ti are found together in many minerals such as polymignite and aeschynite.

Strontium (88) = $CaTi$.

Titanite, an oxide of Ca, Ti, Si, occurs in syenite at Strontian in Argyllshire. This is the locality from which strontianite ($SrCO_3$) is obtained.

Yttrium (88) = $CaTi$.

This element is found in titanite in the syenite of Biellese, Italy. (The difference between Sr and Y is probably due to the two structures given for Ti).

Barium (136) = $SrTi = YTi = CaTi_2$.

Always found with Ca, Sr, and sometimes with Y as in cappelinite.

Columbium (94) = Na_2Ti .

Ti is always found with Cb. The impossibility of completely separating Ti from Cb probably explains why the atomic weight of Cb is so variable and is at present as low as 93.5.

Tantalum (182) = CbY .

Ta is especially associated with Cb and Y in ytrotantalite, sipylite, samarskite, etc.

Tungsten (184) = $CbZr$.

Columbite (a niobate and tantalate of Fe, Mn) is disseminated through the wolframite (a tungstate of Fe, Mn) of Auvergne. Scheelite ($CaWO_4$) and wolframite are commonly found in connection with cassiterite and therefore with zircon. Pyrrhite is a niobate of zirconium. Cb, Zr, and W are found together in sipylite. Fergusonite contains Cb and W, and is found with zircon.

Uranium (238) = $CbYFe$.

Samarskite has been described as mainly a niobate (columbate) of U, Y, and Fe.

Thorium (232) = $CbZrTi$.

Th is especially associated with Cb, Zr, and Ti in aeschynite, polymignite, pyrochlore, etc.

The constitution and structure of the radioactive elements will be fully discussed in relation to the theory as a whole in the next paper, and this will, of course, involve lead, the only one of the heavier elements about which nothing has yet been said.

At present the matter stands as follows: There is one and only one integer for each element in the neighbourhood of its experimental atomic weight, which is especially suitable for explaining the mineralogical and chemical facts with regard to that element. This deduction which has been proved to be true without a doubt applies to all the elements (the twelve rare ones not being available for the investigation). The only exceptions are Gl, Br, Sr, Th, and N. The fact that Gl is apparently an exception is of no importance, because there is evidently something wrong with the data with regard to it, for it is placed in the Periodic Table as a dyad, whilst in *Nature*, Dec. 26, 1901, it is stated that Gl is probably a triad but the Periodic Law stands in the way.

Br is an exception because there are two suitable integers 79 and 81 as previously explained. Probably they are both right as the experimental atomic weight 79.92 is about the arithmetic mean of the two.

Sr has two suitable integers 86 (= Na_2Ca) and 88 ($CaTi$), and as its atomic weight 87.63 is abnormally low considering the Odd and Even Rule, it is probable that both are correct.

Th also happens to have two suitable integers, since it is especially found with Cb, Zr, Y, and Ti.

$CbZrTi = 232$

$CbYTi = 230$

It also happens that the International Committee expect that ionium which ought to be found with Th has an atomic weight less than 232.

Nitrogen is the only real exception, and there is already much experimental evidence that it is an abnormal element (CHEMICAL NEWS, July 18, 1919). Instead of tending to upset the general deduction given above with regard to the other 70 elements, it only serves to accentuate the impossibility of arriving at such a general deduction, if the facts are not really there in order to cause it.

COAL ECONOMY FROM A NATIONAL STANDPOINT.*

By W. H. CASMEY.

WE are wasting coal at the rate of over 50 million tons per year, robbing future generations of their just rights, creating conditions which minimises by two hours per day the sunshine to our cities and towns, assisting in forming our dense winter fogs with their annoyances and expenses, increasing our death rate, and maintaining our present high cost of living, surely sufficient reasons for stamping the subject of coal economy as of national importance.

In the burning of coal which contains other elements besides carbon, the average maximum percentage of CO_2 is 19.2 per cent, due to the fact that all classes of coal contains hydrogen, but in variable quantities, and this gas quickly unites with some of the oxygen and forms watery vapour, leaving of course less oxygen for the carbon in the coal. With one pound of coal and 12 pounds of air, the CO_2 is 19.2 per cent, the furnace temperature 3844° . As this temperature is too high for steam raising purposes, the practice by which the writer has secured the best results, is to allow 50 per cent excess air to the products of combustion, the resulting temperature being 2630° , the CO_2 13 per cent.

If then the CO_2 indicator forms, as it should do, a part of every steam plant, the economical conditions are as easily maintained, other things being equal, as the height of the water in the boilers by means of the pump and gauge glasses.

In everyday practice the percentage of CO_2 seldom exceeds 7 per cent, and taking this figure and the same quality of coal as before, i.e., 12,000 B.Th.U. per pound, 7 per cent CO_2 means 33 lbs. of air per pound of coal, furnace temperature 1510° or 1120° lower, due to having 15 lbs. more excess air per pound of coal, we cannot send the heat away with excess air, and use it for steam raising.

Knowing the desired conditions for burning coal more economically that at present and the immediate benefits which would follow, one can only express surprise at our general apathy; yet we should have no two opinions about a man who

* A Lecture given before the Bradford Textile Society, October 25, 1920.

was constantly grouching about being short of money, if we knew that of every 20/- received he at once threw 5/- away; exactly what we are doing with our coals, only in some cases what we throw away is very much in excess of 5/- in the pound.

Domestic Fires.

In the United Kingdom we have a little over 8 million houses, many thousands of schools, churches, and other public buildings; therefore, the 40 million tons of coal used per year for heating and cooking is well distributed, and after making due allowances for public buildings, the coal consumption per house per year is about four tons, approximately 28 lbs. per house per day.

As an introduction to our Works practice, let us briefly picture the general methods prevailing in our homes.

Under a mistaken idea of economy, we allow the domestic fires to burn until only a few hot cinders remain at the bottom of the grate and then dump on a shovelful of coal, which has the effect of cooling the whole fireplace a long way below the required temperature for igniting the gases, and a stream of smoke is therefore sent up the chimney and by the time the ignition point (900°) is reached, 25 per cent to 30 per cent of the heat value of the coal has escaped.

Defects in Steam Boiler Plants.

If we now turn to the boiler-house, we find about the same conditions as in the management of our domestic fires, and the same remedy is applicable to both, *i.e.*, stoke when the fires are in good condition, clear and bright, and stoke lightly, thereby maintaining a sufficiently high temperature to ignite the liberated gases, which entirely prevents the production of smoke. A suitable motto for room, kitchen, or boiler-house is, "A high temperature is much easier to maintain than produce."

That coal economy is to a large extent governed by the air supply is well known, but the following list also indicates leakages in the majority of our present boiler-houses through which good coal is escaping.

Areas of firegrates and outlets at rear ends of furnace flues out of proportion to area and height of chimney, fires too thin, stoking at the wrong time, stoking too heavily, side dampers not airtight, coal and cinders left in ashes, drag often used when poker would be more good, lack of draught gauges and CO₂ indicators, side and bottom flues too small, boilers and steam pipes not well covered, damp and dirty coal, steam jet blowers, dirty boilers inside and outside, defective circulation and delivery of feed water at the wrong place.

A very interesting list of boiler defects to a nation asking for more coal, a list which has held its own or probably grown since we first commenced to use coal, and about which commissions, Royal and otherwise, have talked, talked, and talked again, but not practised, and for the cure of which hundreds of patents have been granted, the majority of which when applied do more harm than good, and yet we are wasting practically one million tons of precious coal every week, all of which can be saved by stopping the leakages enumerated, in the doing of which there is not the least difficulty.

We have abundant proof that an overall efficiency of 75 per cent to 80 per cent is possible, in fact is now being secured, but in comparison there are thousands of boiler plants to-day giving less than 60 per cent, and one battery of ten boilers tested by the writer gave an overall efficiency of only 53 per cent. Mind, that figure is for boilers and economisers.

Seeing it possible to secure 80 per cent in the one case, why not in all? And it is a question every engineer should ask himself, "Am I doing all I can with this plant, and if so why can others give the same weight of steam for 15 cwts. of coal as I am giving for 20 cwts.?"

(To be continued).

PROCEEDINGS OF SOCIETIES.

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

October 19, 1920.

"Coal as a Future Source of Oil Fuel Supply." By SIR ARTHUR DUCKHAM, K.C.B.

During the War I served under your President, Sir Frederick Black, and I often discussed with him the industrial future of this country. He, therefore, knew that my interests lay very largely in fuel conservation and the heat treatment of coal, and in consequence he asked me to read a paper on this subject to your Institution.

Although getting on in years, I am afraid I am of a sanguine temperament and chose a special phase of this subject, *i.e.*, the obtaining of fuel oil from coal, thinking that I could give a close approximation of the industrial value of the different processes.

With this end in view, I have been making close enquiries of my technical friends, and have been diligently delving into books and pamphlets written by experts.

The conclusion at which I have arrived is, that it is almost impossible to make any definite statement to-day as to the best method of treating coal to obtain the best value in oils and tars. In these circumstances, therefore, I propose to give you a general outline of the situation as I see it, and to make some suggestions as to the most probable line of development.

When we look back to 1914 and compare the industrial conditions then existing with those of to-day, we are amazed. Only six years of time have elapsed since 1914, but to-day we live in a world so changed that more than a generation might have passed.

In view of the great changes caused by the War, it is necessary to free one's mind from old opinions and to formulate lines of progress in accordance with the changed circumstances and altered tendencies.

Preliminary Considerations.

With the growth of civilisation, the needs of the community have become more and more complex. To meet these needs an improved supply of heat, light, and power has been essential.

In past times, wood supplied heat, simple vegetable or animal products provided light, and power was obtained from natural forces, such as wind and water, or by human and animal effort.

As the needs of the community increase in geometrical and not in arithmetical progression, it was soon found that these primitive sources and forms of energy were inadequate. Coal took the place of wood as the source of heat, gas distilled from coal became the source of light, and mechanical power was obtained by harnessing steam generated in coal-fired boilers.

Before the attainment of a supply of mechanical power was obtained by harnessing steam generated in coal-fired boilers.

Before the attainment of a supply of mechanical power, practically unlimited in quantity and application, power had been the least considered of that great industrial and domestic triumvirate—heat, light and power—but rapidly power assumed supremacy.

The discovery and exploitation of the coal measures in Great Britain and the rapid application to industry of the energy so provided gave this country a tremendous start in industrial development. Other countries did not enjoy at that time so favourable a position, constitutionally, geographically, or geologically. North America was naturally the country next best situated for industrial development, being lavishly favoured by Nature and freed from the continual unrest which prevented industrial development on the Continent of Europe.

The discovery of mineral oil in the United States gave a fresh impetus to the production of energy. Used first as a source of heat, and so of power, through the medium of steam boilers, rapidly recognised as a lighting medium, it was only tardily realised that the products of the crude oil, used as a direct power producer in internal combustion engines, provided means of transport which have absolutely revolutionised the domestic and industrial life of the community.

The possibilities of the internal combustion engine working on oil fuel have been demonstrated in the recent War. For the first time, mechanical devices have taken part in land fighting. Man is no longer the unit, but machines, approaching in potentiality the great engines of destruction used in naval warfare, have been utilised and have broken through all human resistance.

Mineral oil, first developed as a ready form of heat and light in the countries where it abounded, was soon found to be so convenient to transport, supply, and apply, that its use became universal. The internal combustion engine has now made oil supplies not only desirable, but indispensable. It has always struck me that it is an extraordinary coincidence that the source of power should also provide the source of lubrication.

To-day there is a world shortage of fuel. The War has closed down many sources of supply. There has been an abnormal upheaval in the position of the workers; the hours of work are shorter and the output per man hour has dropped.

With the growth of the population and the many needs of the community, the railways, especially about towns, have become congested, and the traffic in our streets has become a problem of great difficulty. To-day the community is not obtaining the same quantity of fuel as in pre-War days. On the other hand, the community requires a greater expenditure of energy derived from fuel per head of the population than ever before.

In the past, solid fuel has been transported by rail from the pits through to works and depôts, man-handled to the stores or cellars, again man-handled to the boiler, furnace or grate, burnt wastefully, and then the ashes have had to go through the reverse process. I do not believe future that we shall be able to afford the transport facilities for moving the coal on the congested railway lines leading to large towns. We shall have to restrict the transport of solid fuel and ashes through the congested streets. We shall not be able to afford the labour required for all this work, neither shall we in future be able to obtain labour to perform the arduous work of handling solid fuel, and clearing and removing ashes from boilers, furnaces, or grates. Further, modern practice has already shown the very great advantages of oil fuel for bunkering and for stoking on board ship. Solid fuel must gradually die out for marine work. Oil fuel will take its place. Solid fuel will be displaced for locomotives and our trains will be fired with liquid fuel (and here I may say that, in liquid fuel I include a mixture of solid and liquid fuels in the state commonly known as "colloidal") so that we get a colossal and ever-increasing demand for oil fuel.

Lines of Development.

How is this demand to be met? At the present time there is a shortage of liquid fuel; the demand exceeds supply and is only restricted by high costs. Given a cheap supply of liquid fuel, the demand would increase many times.

It is, however, not possible to think of liquid fuel as the general means of supplying heat and power. On the other hand, I think it clear that the use of solid fuel will die out under the stress of modern conditions, which demand efficiency in the use of labour and the conservation of our national asset—coal.

What other sources of energy are available?

Electricity has proved itself a convenient and economical method of transmitting energy for the purposes of providing light and power, and undoubtedly a cheap supply of electricity generated under economical conditions is a necessity for this country, but no one would to-day consider the generation and transmission of electrical energy for the purpose of providing heat units for general industrial and domestic needs as meeting the case. The average heat economy of electrical generation and transmission to-day does not equal 10 per cent. It is fully realised that this uneconomical figure can be greatly improved on, but it will be many years under ordinary conditions before the efficiency reaches 20 per cent. It is unthinkable to transmit heat units by a method which loses at least 80 per cent of the original heat in generation and transmission.

There remains one other method of transmission of heat units from the coal pit, the source of the fuel supply, to the industrial or domestic user, and that is gas, and it is my belief that the industrial future of this country lies in the conversion of the coal at the pits' mouth into liquid and gaseous fuels. Liquid fuel will be recognised as the medium for providing energy for all transport on land, sea, or air, with the exception of electrical transport for congested areas, while gaseous fuel

will be used direct for the great majority of heating purposes and for the generation of electricity, either by means of steam plants or engines.

Full experience has been gained in America of the transmission of gas over long distances, and there is no question that, starting in the big industrial districts which lie near the coalfields, gas can be supplied in sufficient quantities and can economically replace solid fuel.

The supply of oil for fuel is a necessity. Our only direct source of supply, which would in any way meet requirements, is our coalfields. The late War has proved that oil is indeed the backbone of all military effort. Without oil for lubrication, for transport, for explosives, no nation could possibly continue fighting.

What was once Great Britain's strength has become to a great degree Great Britain's weakness. The submarine has become so great a danger that should another war come, it is possible this island might indeed be isolated and cut off from all outside sources of oil supply. It is therefore essential for national as well as economic necessity to develop supplies of oil fuel at home.

The above brief *resumé* is in my opinion in general terms of the proper line of development. There is in our country at the present time a colossal waste of fuel. By proper conservation we should be able to get the same results with an expenditure of less than half the fuel that is consumed to-day.

It has always seemed a great pity to me that the Government should have been mesmerised by the word "electricity" and the day dreams of the electrical fanatic. They have appointed Electrical Commissioners. They should have appointed Heat, Power, and Light Commissioners, whose duties should be to foster fuel conservation on general lines, and not think only in terms of electricity. I trust that the duties of the Electrical Commissioners will be extended by the Government to embrace those other duties, and that gentlemen here present will use their influence to that end.

For the purpose of this paper I have endeavoured to obtain definite comparisons and figures showing the efficiency of the gasification of coal at the pits' mouth, and the distribution of the gas and liquid fuel to the user in the place of coal, but it is almost impossible to give either a financial or thermal balance sheet for which I could vouch.

There are even difficulties in giving the balance sheets of old and well-tried processes—so many factors are variable. Many balance sheets of new processes have been given from time to time; these have had for their principal object the raising of money from the general public for the flotation of companies, and are therefore not of the character to satisfy a meeting such as this.

Gasworks.

In placing before you the different processes for the heat treatment of coal for the purpose of transforming heat units from solid to gaseous and liquid forms, I would remind you that I have been closely connected with one special form of plant for such purpose for many years, that is the continuous carbonisation of coal in vertical retorts. I have endeavoured, however, to free my mind of all prejudice and I would ask you to take any criticism of existing systems as being made with

the sole purpose of elucidating the problem and endeavouring to obtain the best result for the nation.

The best known method of heat treatment of solid fuel is the carbonisation of coal at the gas works. The prime object of such carbonisation was the manufacture of coal gas for the purpose of lighting, the light being obtained from the luminous flame of the coal gas consumed in a specially constructed burner. Starting as a low temperature process, it gradually became, with the improvement of materials and of construction and advanced knowledge, a high temperature process. The quality of the tar oils obtained changed during this evolution. High temperature meant higher through-puts for the plant, less capital cost, higher yield of gas, less labour and a better financial result, the solid residue gradually finding a ready though somewhat fluctuating market. The discovery of the Welsbach gas mantle and the lowering of the price of the gas, due to improved methods, considerably increased the public demand for gas, while the possibility of using the gas for heating, cooking, and power purposes further increased the importance of the gas supply to the community.

Gas undertakings were, however, greatly hampered by antiquated and restrictive legislation, and were not able to take advantage of the possibilities presented by the new developments in heating, lighting, and power. Further, during the War, the existing restrictive legislation as to raising capital, coupled with high costs, definitely prevented the same advance being made as in other industries. Now that many of these restrictions have been removed or relaxed, it is possible to forecast the immediate lines of gas works development.

There are, roughly speaking, two forms of carbonising plant in use in gas works—horizontal fireclay retorts, charged and discharged by means of machinery, and vertical retorts constructed so that the coal travels continuously through by gravity.

The advantage of the horizontal retorts is that they already exist in most works, have a low capital cost, and can more readily be adapted to treat varying forms of coal. The disadvantages of horizontal retorts are obvious. The large ground space they take up, the arduous conditions which they impose on the workmen, the amount of labour needed, the waste of heat in the discharge of hot coke, and the unavoidable nuisance caused by smoke, dust, and steam in the working operations.

Among the advantages of the continuous working vertical retorts are the small ground space required, the absence of all nuisance, the good working conditions, and the increased make of gas and residuals. The disadvantages are the high capital cost and the fact that the retorts are more sensitive than horizontal retorts to changes of quality in the coal. Vertical retorts can and do carbonise any quality of coal very successfully so long as the quality remains substantially constant, but quick changes from, say Derbyshire to Durham coal, from a light to a heavy caking coal, must of necessity upset the efficiency of the plant and give extra trouble in working.

During the War, the restrictions as to the candle power of the gas allowed to be supplied were relaxed, coal was also scarce and everyone endeavoured to obtain as much gas from coal as

possible. It had occurred to several people before the War that the heat in the coke should be utilised for the formation of water gas by passing steam through the hot coke. During the War it was possible to put these ideas into practice, and remarkable results in continuous-working vertical retorts were obtained. It became possible with steaming to obtain over 20,000 cubic feet of very serviceable gas per ton of coal instead of 12,000. It was further found that the water gas ascending the retort protected the hydrocarbons generated from the coal, and so gave a further increased make of gas and lighter tar oils.

The development of this process is to increase the temperatures about the bottom of the retorts and to highly superheat the steam before it enters the retorts. Further, the hot waste gases from the plant are being passed through waste heat boilers and more than the quantity of steam required for steaming the retorts is obtained in return for a small extra capital expenditure and the cost of the power required to drive the fan on the outlet of the boilers.

There is a distinct limit to the use of steam in vertical retorts. It is not economical beyond a certain point to force heat through a fireclay wall to a charge in the retort for the purpose of making water gas, and although by this means the total gasification of the carbon in the charge has been achieved, the heat and financial balance sheets show this to be uneconomical.

This is undoubtedly the line of advance in gas works practice, but from a national viewpoint I object to the conveyance of the coal to the gas works, and the removal of the coke. The coal pit is the proper place to make gas and pipe lines are the proper means of conveying heat units from the coalfields to the centres of distribution.

As far as oil is concerned, the vertical retort gives better tar oil results than the horizontal retort. Carbonisation of coal in vertical retorts is really fractional destructive distillation. The products of distillation are drawn away as made and have to pass through no higher temperature than that at which they are evolved, whilst if water gas is made at the same time in the retort this process protects the hydrocarbons and gives a greater quantity of a lighter quality tar.

NOTES.

THE idea of distributing samples which has been a feature of so many trade exhibitions in the past is to be carried one step further by the International Advertising Exhibition at the White City towards the end of November. Not merely samples but wares drawn from actual stock have been gifted by manufacturers of advertised articles in such quantities that every visitor who pays the shilling entrance fee will receive something or other out of the free Lucky Dip. To show how heartily the manufacturers of advertised goods are co-operating to make a success of the exhibition—the profits from which will go to charities—one

may note that for the drug trade alone, Sorbo sponges, packets of Price's toilet soaps, Eucryl Tooth Paste, and Pears' Golden series, Schwegge's Table Waters, and Durham-Duplex Safety Razors have been promised in such quantities as to astonish even the organisers. Even newspapers are contributing atlases and free annual subscriptions. The central offices of the Exhibition are at 167, Strand, W.C.2.

AN amalgamation has been completed between English Electric Supplies, Limited, and the Lamp and Supplies Department of Messrs. Siemens Brothers & Co., Limited, and as from November 1, 1920, the business will be carried on under the title of English Electric & Siemens Supplies, Limited. Registered Office: Brook House, 191 and 192, Tottenham Court Road, London, W.1. The Supplies Department with Showrooms and Stores at 38 and 39, Upper Thames Street, London, E.C.2 will be retained, and all orders and business in connection therewith will be dealt with from that address, as heretofore. The same staff will be retained both in London and the Branch Offices. The new company will carry on the business of both companies on the same lines as formerly, and with the same products, with the addition of new electrical devices shortly to be placed on the market. All orders unexecuted, and all obligations entered into by English Electric Supplies, Limited, will be carried out by English Electric & Siemens Supplies, Limited.

THE FUTURE OF WAGES AND PRICES.—The situation in many industries at the present moment is the cause of some anxiety among the public, and discussions are being raised as to underlying economic reasons and practicable remedies. In view of the fact that many conflicting opinions are being expressed, the Federation of British Industries has drawn up a statement on the "Future of Wages and Prices," pointing the way to the only course which, in its opinion, can lead to the solution of the difficulties which beset the nation. The chief heads of the statement comprise the effect of the war on prices, "real" value of wages, reduction of prices (two alternatives), the illusion of Government price fixing, rapid deflation impossible, the importance of increased output, the division of the product of industry, and world exhaustion. The F.B.I. regard the only effective means by which prices can be reduced and the real wages of labour improved to be by working the existing instruments of production at their maximum pressure, and so increasing as rapidly as possible the mass of commodities to be bought. Any attempt on the part of the workers to improve their conditions by a 'canny' and similar methods not only fails in its object, but, by causing a rise in prices, actually reduces the purchasing power of their present wages. An increase in money wages may temporarily alter this state of affairs, but it cannot affect the final result. It is true that the workers in one trade may secure an improvement in their own position at the expense of the rest of the community, but if the wages in all trades are increased, this merely results in the re-establishment of the old value of wages at a correspondingly increased level of prices.—*The Chemist and Druggist*, October 16, 1920.

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ROYAL INSTITUTION.—A General Meeting of the Members of the Royal Institution was held on the 1st inst. Sir James Crichton-Browne, Treasurer and Vice-President, in the chair. The Secretary reported the deaths of Professor Armand Gautier, an Honorary Member, and of Professor John Perry, and resolutions of condolence with the relatives were passed. Commander R. B. Brooks and Mr. J. F. Dalton were elected Members.

WE learn with regret from the Locomotive Department of the L. & N.W. Railway that Mr. C. J. Bowen Cooke, C.B.E., has died at Falmouth after a short illness, in his 62nd year.

MEETINGS FOR THE WEEK.

Monday, November 8.

Biochemical Society.
Society of Chemical Industry. (At Leeds).
Royal Geographical Society, 8.30.

Tuesday November 9.

Mineralogical Society, 5.30.
Institute of Metals, 8. (At Glasgow).

Wednesday, November 10.

Conjoint Board, 3.

Thursday, November 11.

Royal Society, 4.30. "Calcification of the Vetrebral Contra in Sharks and Rays" by W. G. Ridewood, D.Sc.
"Studies in the Mechanism of Enzyme Action. I. Role of the Reaction of the Medium in fixing the Optimum Temperature of a Ferment" by A. Compton, D.Sc.
"Effect of certain Dietary Deficiencies on the Suprarenal Glands" by C. H. Kellaway.
"The Genetics of Sex in *Funaria hygrometrica*" by E. J. Collins.
Institute of Chemistry. (At Liverpool).
Institution of Electrical Engineers, 6.
Optical Society, 7.30.

Friday, November 12.

Institute of Chemistry, 4.
Physical Society, 5.

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THE PHYSICS AND CHEMISTRY OF COLLOIDS AND THEIR BEARING ON INDUSTRIAL QUESTIONS.

A SHORT SURVEY OF THE PHYSICS AND CHEMISTRY OF COLLOIDS.

By DR. THE SVEDBERG, Professor of Physical Chemistry, University of Upsala.

(Concluded from p. 219.)

Finally we will consider two phenomena, the study of which does not, it is true, enable us to carry out direct measurements of the structure, but which, in spite of that, are of great interest in judging of the structure of colloids, viz., the viscosity on the one hand, and, on the other, the adsorption and the accompanying phenomena, viz., the cataphoresis and the electric endosmose.

The viscosity of a sol depends, in a manner not yet known, on the size of the particles, the concentration, &c., but above all on the nature of the particles. Some sols, e.g. metal hydrosols, suspensions of barium sulphate (Case 1) have a viscosity only slightly greater than that of water, but others, e.g. silicic acid hydrosol, oil emulsion, gelatin solution (Case 2) have a viscosity many times greater than that of water. From the fact that suspensions with undoubtedly solid particles come under Case 1 and emulsions with undoubtedly fluid particles come under Case 2, the conclusion has been drawn that the fine-grained colloids under Case 1 also contain solid particles and those under Case 2 fluid ones. If this be the case, measurements of the viscosity would be a capital means of ascertaining the state of aggregation of the substance of the particles. Recent investigations indicate, however, that the case is far more complicated. Small particles probably have relatively thicker water-coverings than greater particles, and, accordingly, the viscosity is higher in a fine-grained colloid than in a coarser one, provided the two sols have particles of the same material and are of the same concentration by weight (e.g., sulphur hydrosols). When the potential difference between particles and fluid is altered the thickness of the water-coverings should alter and, as a matter of fact, the viscosity is altered too. As the water-covering increases, the particle will act more and more like a drop of fluid in relation to the surrounding medium and will, therefore, as far as the viscosity is concerned, approach more and more to the limiting case which is represented by an oil emulsion.

The phases—two or more in number—in a disperse system have a contact surface very large relatively to the volume of the system. It is obvious that in such circumstances adsorption plays a prominent rôle. The adsorption of different substances differs in strength. If an electrolytically-dissociated salt is adsorbed, cations and anions are, of course, brought together at the contact surface in equal numbers, but the adsorption of the particles in relation to cations and

anions is most often unequal, inasmuch as one is present in excess nearest to the surface of contact, and the other in excess some way out in the liquid. The result is the formation of an electrical potential difference, a so-called adsorption potential difference or an electrical double-layer. Because of this the disperse phase, when exposed to the influence of an electric field, will migrate towards one of the poles, provided it is freely movable, as in the case of a colloid solution (cataphoresis). If the disperse phase is immovable the liquid will move in the opposite direction (electrical endosmose). By measuring the velocity of migration of the particles or the liquid under various conditions we are able to study the changes in the difference of potential and thereby in the adsorption. At least at low concentrations the adsorption may be expressed by the formula

$$y = a \cdot e^{\beta}$$

where y is the amount of substance adsorbed per gr. adsorbent, e the concentration in the solution of the substance adsorbed, and a and β constants depending on the nature of both. Now, as a rule, it happens that for the two ions of a salt both a and β have different values, e.g.

$$\begin{aligned} a & \text{ cation} < a \text{ anion} \\ \beta & \text{ cation} > \beta \text{ anion} \end{aligned}$$

In the example chosen the disperse phase will with increasing adsorption become more and more negative in relation to the dispersion medium. This charge reaches a maximum and decreases to zero, at the point where the adsorption isotherms intersect, then becomes positive and increases again.

The changes of state which may occur in a disperse system, a colloid, are essentially changes of structure. Of course, purely chemical reactions too, are to be taken into consideration, but they do not play such a prominent part here as in the molecular structural systems. The greater number of the disperse systems, and those of greatest importance too, are the ones whose disperse phase is embedded in the other phase in the form of particles; in the sequel we will only mention the changes of state in such systems. The most important change of state is the uniting together of the single particles (primary particles) into aggregates (secondary particles). Such an aggregation often occurs directly after the formation of the particles. It may stop for various reasons after the aggregates have reached a certain size. The result is a colloid with complex particles—a *secondary colloid*. If the aggregation goes on further we may have two extreme possibilities—with many transition forms.

First Case: One or more of the following factors dominate, viz.:—

- (1) Low hydration of the particles.
- (2) Low number of particles per unit volume.
- (3) Great difference in specific gravity between particles and liquid.
- (4) Violent stirring of the system.

The characteristic of this case is that no bridges are formed between the aggregates and that, in consequence of this, they fall to the bottom after having grown sufficiently; *the colloid is precipitated* (e.g. coagulation of a gold hydrosol by the addition of hydrochloric acid).

Second Case: One or more of the following factors dominate, viz. :—

- (1) High hydration of the particles.
- (2) High number of particles per unit volume.
- (3) Small difference in specific gravity between particles and liquid.
- (4) No stirring of the system.

In this case bridges are formed between the aggregates, and the particles arrange themselves into a three-dimensional network throughout the system: *the colloid gelatinises* (e.g. the coagulation of a sol of silicic acid by the addition of hydrochloric acid, the setting of a warm gelatin solution when cooling). Owing to capillary forces the liquid is kept in the network with great strength. Measurements have shown that the liquid is under a pressure of several hundred atmospheres. In many respects, therefore, the gelatinised colloid acts as a solid.

There exist numerous transition forms between these two extreme cases. If the particles are not bound together by bridges into a solid, but still reach macroscopical size and possess a certain loose structure, one speaks of *flocculation of the colloid* (e.g. coagulation of ferric hydroxide hydrosol by addition of ammonia). It may be doubted, however, if such flocculent suspensions are not to be regarded as fragments of a gel of little mechanical resistance shattered by the stirring of the liquid. Several observations support the view that there is in all colloids a certain tendency towards the formation of a network structure, the network being, however, in such systems as approach Case 1, very easily destroyed by movements in the liquid. In Case 1 the Brownian movements alone of the particles should suffice.

The most important cause of the aggregation of the particles is the decrease or the disappearance of the difference of potential between particle and liquid. This may be effected by altering the ion adsorption. Hence one of the most important means of bringing about aggregation or disaggregation is: *addition or removal of ions*. Because of the opposite electric and coagulating action of anion and cation and their difference of adsorption there will always exist, for certain electrolytes in relation to a certain colloid, a domain of concentration within which they have a disaggregating action. If a solely aggregating electrolyte is added to a colloid in increasing doses (e.g. hydrochloric acid to a gold hydrosol), the velocity of aggregation first rises rapidly with concentration, then more slowly and reaches a constant maximum value. Let us make the assumption that within the latter region *every* mutual approach of two particles to a certain limit leads to aggregation, but within the former region only a certain *fraction* of those approaches. Then it is possible to develop, on the basis of the laws of the Brownian movements alone, a mathematical theory for the kinetic of aggregation. The formulae for the decrease in the number of single particles (primary particles), and for that in the total number of particles (primary particles + aggregates) have been verified experimentally.

We have—

$$v_1 + v_2 + v_3 + \dots = \frac{v_0}{1 + \beta t}$$

$$v_1 = \frac{v_0}{(1 + \beta t)^2}$$

where—

v_0 = original number of particles.

v_1 = number of single particles after the time t .

v_2 = number of double particles after the time t .

v_3 = number of triple particles after the time t .

$\beta = 4\pi DRv_0$

D = the diffusion constant.

R = the distance to which the particles must approach if there is to be any aggregation.

With regard to the aggregation by electrolytes it has, in addition, been found that inorganic ions of the same valency generally aggregate equally strongly if added in equivalent amounts. This is due to some extent to their being nearly equally strongly adsorbed. When the valency of the aggregating ion increases the aggregating effect rises very rapidly. The concentrations of the ions K⁺, Ba²⁺, Al³⁺ ... required to aggregate particles of As₂S₃ to the same degree show the mutual relations: 1, 1/20, 1/1000. Thus the three-valent Al³⁺ ... has an aggregating power 1000 times greater than the mono-valent K⁺. These circumstances are closely related to the course of the adsorption isotherm, but are not yet quite clear.

The aggregation may be reversible or irreversible, i.e., in certain cases disaggregation may be effected, in others not. Some colloids (e.g. metal hydrosols) are difficult to disaggregate, others (e.g. sulphur hydrosols) are easy. Certain ions nearly always bring about irreversible, others reversible aggregation. The question of irreversible or reversible coagulation is probably closely connected with that of the hydration of the particles. Thus particles which hold much water around them are easily disaggregated. The water-covering prevents the particles from uniting too closely together.

The aggregating effect of an electrolyte may often be reduced to a very great extent by the addition of a small quantity of a suitable colloid of another kind only slightly sensitive to electrolytes, a so-called protective colloid, e.g. gelatin to a gold hydrosol. As a rule the electric charge of the protective colloid should be of the same sign as that of the colloid to be protected. The mechanism of this protecting action is still but very incompletely known. Most probably the particles of the protective colloid become attached to the particles of the other colloid and the aggregate resulting from this obtains a good deal of the stability towards electrolytes which characterises the protective colloid. Colloids of opposite electric charge precipitate each other mutually (e.g. the negative Sb₂S₃ and the positive Fe₂O₃) provided there is not too great an excess of either of them, in which case no precipitation will occur. This is obviously entirely analogous to the action of the ions. Such mutual colloidal reactions are of great importance in the economy of nature and in industry.

In the preparation of easily aggregated colloids a protective colloid is often added in order to maintain the primary structure. Thus the particles of a metal hydrosol, if formed in the

presence of a small quantity of a protective colloid, are kept apart even when the sol is evaporated to dryness. The dry substance can be redissolved in water without any perceptible change of structure taking place (e.g. commercial colloid silver).

A change of structure that plays a part, formerly a little overrated, in colloid solutions with comparatively easily soluble particles is the growth of the larger particles at the expense of the smaller ones. In a suspension of calcium sulphate this change of structure is clearly visible, but in the more sparingly soluble barium sulphate the process goes on at an extremely slow rate. Formerly, aggregation, especially the irreversible process, was often interpreted as a recrystallisation. In irreversible aggregates as well as in compressed powders there gradually take place association and crystallisation phenomena which may greatly change the structure of the system (e.g. silver crystals in sediments from silver colloids).

Processes of the latter kind play a prominent part, especially in gelatinised colloids. On the whole a great variety of changes in structure and accompanying processes may occur in gels. When gradually deprived of water the gel of silicic acid, for instance, goes through a series of states, some of which differ rather decidedly from others. The nature of these processes is not yet known. A gelatin gel probably consists of particles with a high percentage of "dry substance" and a liquid with a low percentage. In sol-formation water is supposed to pass over from the liquid to the particles, the particle-associations being thereby disintegrated; in the gel-formation the particles lose water.

In the study of the changes of structure and of the properties of secondary sols and gels we use, at least to some extent, the same methods as in the study of sols. Thus aggregation may be followed in the ultramicroscope, by sedimentation observations, by means of measuring the light-adsorption, the double refraction in magnetic and electric fields, the viscosity. The most reliable method consists, of course, in direct countings of the particles in the ultramicroscope. But it is not always possible to carry out these countings. The viscosity is a very sensitive indicator of changes in structure, especially within the organic colloids. The values we arrive at when measuring the viscosity of an aggregating colloid are, however, dependent to a great extent on the state of current in the system and, consequently, on the kind of method employed for the measurement. The microscopic aggregation process is accompanied by a building up of a macroscopic network and the mechanical resisting power of this network determines, to a considerable degree, the viscosity measured by the experimenter. The aggregation may lead to the formation of secondary particles of a more or less high degree of dissymmetry. This can be studied by measuring the change which the double refraction of the sol in a magnetic field undergoes during the progress of aggregation.

The study of the structure of gels is a rather difficult one. The particles of most gels do not contrast optically to any great extent with the surrounding medium and consequently the ultramicroscope is not able, as a rule, to make their primary particles visible. Moreover, these are

often packed together so closely that they cannot be distinguished from one another optically. On the other hand, we have been able to study with more success the macroscopic properties of the gels in chemical and physical respects. The elastic gels, especially gelatin, collodion, celluloid, rubber, &c., play a prominent part in industry, and their investigation is therefore a matter of great importance.

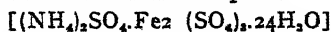
DETERMINATION OF MOLYBDENUM.

By J. P. BONARDI and EDWARD P. BARRETT.

(Continued from p. 209.)

Precaution Against Fading End Point.

IN titrating the molybdenum solution obtained from an ore high in silica that had been fused, the end point vanished. This result may have been due to the presence of silica and other salts in the solution, which perhaps retarded the reaction, because fading did not occur when pure MoM_2 or ammonium molybdate, or the solution prepared by the acid-digestion method, was titrated. In order to overcome this difficulty a titrating mixture was made as follows: 100 grms. of pure ammonium ferric sulphate



was dissolved in one litre of pure water; this was mixed with one litre of solution containing 90 grms. of manganese sulphate, 175 cc. of syrup of hypophosphate (H_2PO_4), and 175 cc. of concentrated sulphuric acid. The phosphoric acid renders the solution colourless. 50 cc. of this mixture would be equivalent to approximately 0.275 grm. Fe, or 0.1584 grm. Mo, and would be sufficient for an ordinary molybdenum determination. The use of this solution in the receiver of the reductor tended to give a sharper end point, as is true when a reduced iron solution is titrated in the presence of a titrating mixture. On the other hand, a larger blank subtraction was necessary in each run. This applied to small or large amounts of molybdenum in solution and may have been partly due to some ferrous iron being present in the titrating mixture, or to other causes as given under "Effect of Blank" (p. 14). The indications are that a blank obtained without using a titrating mixture in the receiver is due mostly to causes other than dissolved ferrous iron. The following explanation will make this statement clearer.

Fifty cc. of titrating mixture in 250 cc. of water required 0.50 cc. of one-twentieth normal permanganate, whereas 50 cc. of titrating mixture in the Jones receiver, followed by a blank run, required 0.80 cc. of the permanganate. 25 cc. of a molybdenum solution, as was shown under "Effect of Blank" required 41.30 cc. of permanganate solution, whereas when the titrating mixture was used the permanganate reading was 42 cc. Therefore, a blank must be subtracted when a titrating mixture is used in the receiving flask. 1 cc. of molybdenum solution required 1.85 cc. of permanganate without the mixture and 2.60 cc. with the mixture in the receiver. Thus the use of this solution in the receiver was of no special advantage with the strengths of solution titrated, although many analysts claim that its use

is absolutely necessary to prevent the reduced molybdenum from being oxidised and to give a sharper end point. Reduction or oxidation gave no trouble in titrating solutions from low-grade ores of not more than 10 per cent molybdenum content, when the extra length of reductor was used as directed.

The end point, however, can easily be checked by passing the solution through the reductor a second time, which should give the same result as passing the solution through once. The bright green colour indicates a complete reduction. The molybdenum solution should be titrated immediately; if it is allowed to stand, ferric phosphate solution should be used in the receiver, as recommended by Randall (D. L. Randall: "The Behaviour of Molybdic Acid in the Zinc Reductor" *Am. Jour. Sci.*, 1907, ser. 4, xxiv., 313). This point is also discussed in several standard text books (F. A. Gooch: "Methods of Chemical Analysis," 1912, p. 424; W. W. Scott: "Standard Methods of Chemical Analysis," 2nd ed. rev., 1917, p. 281).

Precautions for High-Grade Ore.

In working with higher grade material, carrying more than 10 per cent molybdenum, use of the ferric phosphate solution is recommended, as this would prevent reoxidation of a strong reduced molybdenum solution on exposure to the air, and would also give consistent results for any low-grade material analysed. For experienced chemists, this precaution is not absolutely necessary, but its observance would perhaps be advisable for beginners.

A great deal has been written and many discussions have taken place concerning the state of reduction of the molybdenum after passing through the reductor. This controversy has been taken up in detail by Randall (D. L. Randall, work cited) and the reduction of the molybdenum to MoO_3 has been proved conclusively.

If the volumetric method is used for assaying ores containing more than 50 per cent MoS_2 , a large sample should be digested and an aliquot portion should be taken, besides a stronger solution of potassium permanganate than 1/20 normal should be used. However, the error even in such a determination must be multiplied by the factor for the aliquot portion taken that corresponds to a 1-grm. sample in order to calculate the true percentage. With the gravimetric method, the chances of error in working with aliquot parts are small for high-grade material as a larger sample could be taken for analysis than in the volumetric method. A further advantage of the gravimetric method is the small factor (0.2615) that is used in multiplying the weight of lead molybdate to obtain the weight of molybdenum.

Precautions with Ferromolybdenum.

The sodium peroxide fusion method can be used in the determination of ferromolybdenum with the special precaution that after filtration the precipitated hydroxides must be redissolved, reprecipitated, and thoroughly washed. Ferric phosphate solution should be used in the receiving flask of the reductor to guard against oxidation of the strong reduced molybdenum solution.

Limit of Accuracy.

In the check determination for the volumetric method in the analyses given, and in many other

analyses that were made, a difference of 0.20 cc. for duplicates on the same sample was not uncommon. This difference, when calculated against 1/20 normal permanganate represents 0.032 per cent Mo, or a weight of 0.00032 grm., on the basis of a 1-grm. sample. This percentage would, no doubt, be about the limit of accuracy in comparing checks for molybdenum that was determined as the sulphide and ignited to MoO_3 and weighed. In the ignition method the separation of the sulphide from all other elements, especially copper, and the necessary accurate ignition to MoO_3 is unsatisfactory and uncertain, and must be attended with much precaution, particularly with low-grade material. This point is discussed in detail under the procedure for the gravimetric method. The difference between the molybdenum determined gravimetrically as lead molybdate and the molybdenum determined volumetrically by lead acetate titration, with tannic acid as an outside indicator, was 0.0003 grm., which for a 1-grm. sample would represent 0.03 per cent; however, if the solution titrated represents a large sample, 2 to 5 grms., the limit of accuracy is 0.01 per cent or less, is the same as in the permanganate titration.

Summary and Conclusions as to Volumetric Method.

1. Decomposition with sodium peroxide is for low-grade ores the most rapid and reliable fusion method for obtaining molybdenum in solution.
2. The Jones reductor must be prepared and used according to the directions given herein in order to obtain accurate results.
3. The size of sample desirable for analysis and the strength of potassium permanganate used in titration depends on the grade of ore tested.
4. A correction factor should be applied to the titration result in order to counteract the "blank effect."
5. The limit of accuracy for the method is within 0.01 per cent on the basis of a 1-grm. sample, if attended by the proper procedure.
6. Interfering elements found in molybdenum ores can be removed or determined.
7. The molybdenum in high-grade ores and in ferromolybdenum can be determined by this method if the proper precautions are taken.

Gravimetric Determination of Molybdenum by Precipitating and Weighing as Lead Molybdate.

The following procedure has proved to be rapid and accurate for the analysis of low-grade materials. The method is fundamentally that outlined by Scott (W. W. Scott: "Standard Methods of Chemical Analysis," 2nd ed. rev., 1918, p. 278), in which he quotes the method of Chantard (T. M. Chantard: "On the Determination of Molybdic acid as plumbic molybdate," *Am. Jour. Sci.*, 1871, ser. 3, i., 416), but special attention is called to the details.

The ore is decomposed with acids and treated with ammonium hydroxide to form ammonium molybdate. From the hot solution the molybdenum is precipitated as PbMoO_4 by adding lead acetate solution in 2 or 3 cc. excess, heating the mixture a few minutes, and filtering. The precipitated lead molybdate is then ignited, cooled, weighed, and the weight of molybdenum is calculated.

Procedure for Acid Decomposition.

Weigh 0.25 grms. of the finely pulverised ore into a 250 cc. Erlenmeyer flask. Add 15 cc. of nitric acid and heat until the brown fumes are gone. This is the most rapid manner of decomposing the sulphides present. Carefully add 5 to 10 cc. of hydrochloric acid and heat about 20 minutes or until the ore is completely decomposed. Then evaporate to dryness, moisten with hydrochloric acid and wash down the sides of the flask with hot water and heat about 5 minutes longer. Cool the mixture, add 5 to 10 cc. excess of ammonium hydroxide, heat a few minutes, and filter hot, washing with hot water at least 5 times. Puncture the filter paper and wash the residue of insoluble material (iron and aluminium hydroxides) into the Erlenmeyer flask, add sufficient hydrochloric acid to dissolve the precipitated hydroxides, make the solution slightly ammoniacal, heat, and filter into the same beakers that were used for the first filtration. Wash well with hot water. This second treatment is made in order to prevent an appreciable amount of molybdenum from being held mechanically in the residue.

The Removal of Lead.

If the ore carries lead, as wulfenite, decompose with nitric acid and hydrochloric acid as previously stated, but after cooling add 10 cc. of sulphuric acid and evaporate to dense fumes. Cool, add about 50 to 60 cc. of water and heat to dissolve the soluble sulphates. Cool, filter to remove the insoluble material and lead, wash well, and add to the filtrate 5 to 10 cc. excess of ammonium hydroxide; heat and filter. Repeat this precipitation in order to extract all the molybdenum from the residue.

The Removal of the Phosphorus.

Phosphorus, when present, should be removed by the addition of a few cc. of magnesia mixture to the ammoniacal solution before filtering off the iron and aluminium hydroxides. The ammoniacal solution should be warmed about 20 minutes to allow the precipitated magnesium phosphate to settle. If not removed, the phosphorus will precipitate as lead phosphate with the lead molybdate.

Further Preparation of the Solution.

The molybdenum is now in the form of ammonium molybdate in a solution practically free from silica, iron, and alumina, also lead if the sample was evaporated to fumes with sulphuric acid.

The volume of the solution should approximate 250 cc. Acidify the solution with hydrochloric acid, using methyl orange as an indicator and adding about 5 cc. excess acid. The use of hydrochloric acid in neutralising is preferred to nitric or acetic acid because the presence of ammonium chloride will hold in solution many of the third and fourth group elements that might otherwise be precipitated with the lead molybdate; besides, chloride salts are more highly ionised than the acetates and hence are stronger electrolytes and tend to prevent formation of colloids. Add 5 to 10 grms. of sodium or ammonium acetate to destroy any free mineral acid. The use of hydrochloric acid and the acetate causes the lead molybdate to precipitate in a granular form, to settle

rapidly, and to be easily filtered and washed. Weiser (H. B. Weiser, "The Physical Character of Precipitated Lead Molybdate and its Importance in the Estimation of Molybdenum and Lead," *Jour. Phys. Chem.*, 1916, xx., 640-62) recommends the addition of 8 drops of nitric acid before precipitating the molybdenum.

Precipitation.

The precipitation is best made by titrating the hot molybdenum solution with a lead acetate solution (about 18 grms. of crystallised lead acetate per litre) until a test drop gives no colour change with a drop of tannic acid solution. Add about 2 cc. of excess lead acetate, 2 or 3 cc. of acetic acid, and replace the beaker on the hot-plate, keeping the contents just below the boiling point for about 15 or 20 minutes or until the precipitated lead molybdate has crystallised and settled. Filter hot and wash well with hot water. If any colloids run through the paper the washing should be stopped in order to prevent further loss from colloidal lead molybdate running through the paper. If the precipitate is bulky, wash with a 2 per cent solution of sodium or ammonium acetate in order to decrease the possibility of colloidal lead molybdate forming. Weiser (A. H. Weiser, place cited) suggests that the precipitate be washed twice by decantation with a 2 per cent solution of ammonium nitrate and then transferred to the filter paper and washed with hot water. The precipitated lead molybdate will be very pure.

The washed filter is placed in a fire-clay annealing cup and ignited at a dull red heat in a muffle (W. W. Scott, "Standard Methods of Chemical Analysis," 2nd ed., 1917, p. 278). The filter need not be previously dried. After cooling, the precipitate is brushed out of the annealing cup on to the balance pan and weighed. The weight of the lead molybdate times 0.2615 gives the weight of the molybdenum.

(To be continued.)

COAL ECONOMY FROM A NATIONAL STANDPOINT.*

By W. H. CASMEY.

(Concluded from p. 223.)

The Lancashire Boiler.

THE Lancashire boiler, introduced over 100 years ago, stands out even to-day as one of our most valuable inventions, and was of the greatest assistance to the early industrial life of this country. Had our ancestors considered boiler duty efficiency and the value of coals more than ease in boiler construction, an enormous weight of coal would have been saved, instead, however, after using the original Lancashire boiler for 60 years, contracted flues were introduced and expanding coal wastage, then as a natural result commenced and still continues.

Like many others interested in steam practice, the writer has taken for granted the generally expressed opinion, that the Lancashire boiler as made to-day was the joint invention of two then well-known engineers, Fairbairn and Hetherington and brought out by them in 1844, but in reading up for the present paper the desire to make

* A Lecture given before the Bradford Textile Society, October 23, 1920.

further investigations on the subject of boilers became insistent, and the following summary of notes collected from nearly 20 different writers will be interesting.

Prior to 1811, the Cornish boiler was the principle steam generator in use, but during that year the first twin-flued boiler was introduced, the furnace flues of which, like the single flue in the Cornish boiler, were of the same diameter from end to end and this is the boiler to which the name Lancashire boiler was given.

Between 1811 and 1820 several types of Tank boilers were introduced, all with parallel furnace flues, and in 1859 a further two-flued boiler was introduced, the setting being much the same as we are practicing to-day.

In 1872, the Fairburn Engineering Company placed a twin-flued boiler on the market which, like all its predecessors, had two straight furnace flues, and the following year a boiler fitted with contracted flues exactly the type we are making to-day and known far and wide as the Lancashire boiler was introduced, whereas the true Lancashire boiler has parallel flues and was introduced in 1811.

During the last few years we have replaced many old boilers fitted with parallel flues, two of such, 8ft. in diameter, are now in our yard, the flues 3ft. diameter, 2ins. less at the front end than in the same diameter modern boiler, and 4ins. larger in diameter at the back end, but this old type will evaporate 15 per cent more water per hour than one of our present design under exactly the same conditions.

To prove this statement let us assume that each boiler was operated by a suction equal to 1200 feet per minute at the rear ends of the boiler; the old boiler offers 14 square feet to this suction, the modern boiler 11.2 square feet, the old boiler has an air supply sufficient to burn 1116lbs of coal per hour and taking 8lbs. of water per pound of coal give an hourly evaporation of 8928lbs.

The modern boiler has only air supply for burning 942lbs. of coal, and at the same rate of evaporation per pound of coal the hourly duty will be 7856lbs., from which it is clear that six Lancashire boilers as made 109 years ago will evaporate as much water as seven boilers of the same diameter of present-day type, this is not progress.

No matter how powerful the suction of a boiler chimney may be its useful effect is governed by the distance the gases have to travel and the smallest sectional area through which they have to pass between the furnaces and the chimney and the restricted area in our modern boiler is the contracted rear end of the furnace flues.

From the above it is clear a relationship exists between the grate area of a boiler and the area through which its gases escape and in the old type the ratio is 2.57 to 1 and in the modern boiler of equal diameters 3.5 to 1, the respective evaporation per square foot of grate being 240lbs. and 197lbs.

Look at our Lancashire boilers as made to-day, standard length 30 feet and diameters ranging from 7 feet to 9 feet and upwards, grates in all boilers 6 feet long, and furnace flues contracted at the rear end 6 ins. and the practical results under such conditions are that a boiler 7 feet diameter requires 4 square feet of grate to evaporate

as much water as can be done with a 9 feet diameter boiler with 2.7 square feet.

If boilers 7 feet, 8 feet, and 9 feet diameters were worked with equal draught, the respective evaporations per square foot of grate would be 144lbs., 184lbs., and 238lbs., but if the grates were modified until the ratio of grate to outlet was 2 to 1 in each boiler, the evaporations in all three would be equal, say 312lbs. per square foot of grate, the whole subject of modified grates is however explained in my booklet on Coal Economy, recently published by Charles Griffin and Co., London; the book was specially written for firemen and enginemmen.

As indicating the new known weakness of our present so-called Lancashire boiler, the subject of 2 to 1 ratio of grate to gas outlet was submitted to the Ministry of Munitions Inventions in August 1919, and in November of the same year an Award was received for it.

"We backed the wrong horse" in taking on the boiler of 1873 with contracted flues instead of holding on to the straight-flued boiler of 1811, but we cannot now without great expense increase the diameter of our present boiler flues at the back end to secure the 2 to 1 ratio; we can, however, secure it by merely reducing the area of our furnaces and share in the value of the idea as the following extracts from letters received indicates what others are doing.

(a) We have four Lancashire boilers 30 feet by 8 feet fitted with coking stokers and induced draught; we have cut down our firegrates from 6 feet to 3 feet 10 ins., and reduced our coal consumption over 700 tons per year.

(b) Our plant consists of two Lancashire boilers 30 feet by 9 feet, fitted with sprinkling stokers, length of grates 3 feet 6 ins., with a dead plate behind the bars 2 feet 6 ins. long. Our engines develop 800 h.p. Class of fuel: rough slack; evaporation per pound of slack, 9lbs.

(c) We have three Lancashire boilers 30 feet by 8 feet, grates have been cut down from 8 feet, 6 feet 6 ins. to 4 feet; the practical effect has been a saving in coal of 20 per cent.

(d) We have one Lancashire boiler 30 feet by 8 feet, and by cutting down the grates from 6 feet to 4 feet we have reduced our coal consumption 140 tons per year.

(e) A firm of Lancashire manufacturers writes: "Since cutting down our boiler grates one-third as advised by you we have saved 10 per cent in fuel and stopped black smoke."

(f) Since reducing the grates in our 28 feet by 7 feet 6 ins. Lancashire boilers from 6 feet to 3 feet 9 ins. 18 months ago, we have reduced our coal consumption two tons per week.

(g) In our own works the grates of the 30 feet by 8 feet boiler have been reduced one-third and the savings effected exceeds one ton of coal per week.

Coal Saving Suggestion.

Having indicated the chief causes of coal wastage, and over which the fireman at present has but little control, we may now consider some of the minor details of wastage he can control, with suggestions as to how they can be removed.

A poor draught necessitates thin fires and constant use of the firing tools, which allows fuel to fall into the ashpit and allows a large supply of excess air, and therefore a low boiler duty and

efficiency is the result; the trouble can generally be overcome by reducing the length of grates on the lines mentioned, which enables thicker fires and less air, consequently a higher furnace temperature and increased duty and efficiency.

A fire should not be less than 10 ins. thick, and maintained at its highest efficiency by stoking lightly when the fires are clear and bright, the stoking to be on the sides alternatively, as this gives the necessary temperature to ignite the gases as liberated, and heat is then produced instead of smoke.

The brickwork of the external flues of boiler and economiser should be inspected daily, and any indication of leakage of air should be pointed up at once, and side dampers should be made air-tight either by packing or adopting air-tight damper covers.

When fuel is used which has a tendency to coke, use the poker to lift the fires lightly and thus allow air to reach the body of the fires, the drag or rake with such fuel not only makes smoke but wastes more coal than any other tool used in the boiler-house.

It is no uncommon thing to find the ashes drawn from underneath a furnace containing 50 per cent of small coal and cinders; this is impossible if discretion is used with the firing tools and thickness of fires; the small ashes in well-managed works are reburned.

In a battery of boilers it is a very common occurrence for the boiler nearest the chimney to be burning more fuel than the one at the opposite end of the range, if, however, all the boilers were fitted with draught gauges the dampers could then be so regulated that each boiler does its share of the work or in case the downtake of any boiler gives way thus allowing the gases to escape direct to the main flue, the draught gauge would at once indicate this by showing reduced suction on the side flues.

It is an interesting fact that knowing about 80 per cent of the heat taken up by the boiler is received from the first 7 feet or 8 feet of the furnace flues, and yet we deliver the feed water into that section of the boiler where ebullition takes place. Is it not clearly evident the water should be delivered below the flues and then as it slowly rises it is gradually being qualified, *i.e.*, charged with the necessary heat units to produce steam?

Boiler Seatings.

Standardisation is the one thing required in the boiler-house, both in design of boilers, their furnaces and gas outlets, and also in the external flues, and the following data from our own practice may assist in that direction.

The depth of the bottom flue of any diameter of boiler should be half the diameter of the boiler and the width half the diameter plus 6 inches.

Side flues one-seventh the diameter of the boiler.

Distance from back end of boiler to face of brickwork forming the downtake equal to diameter of one furnace flue front end, distance from top of bridge to crown of flue one-third diameter of flue.

Division walls between boilers 16 ins. thick, including a 2-inch space in the centre filled with fine dust and all external walls should have similar dust spaces, the effect of which is to reduce to

a minimum, heat losses through the brickwork.

By standardising boiler grates, gas outlets, and settings as described, the sectional area and height of chimney can at once be given when the evaporation required is stated.

As an illustration, consider a 30 feet by 9 feet boiler with modified grates 35 square feet of outlet from furnace flues is $17\frac{1}{2}$ square feet and 3 square feet at this point required 1 square foot of chimney area, therefore sectional area of chimney 6 square feet, say 2 feet 9 ins. diameter.

The height of the chimney for any given coal consumption is even more easily arrived at than its sectional area; if it is desired to burn 900lbs. of coal per hour, cut off the right-hand figure, the remainder, 90, is the height of the chimney in feet; say for 1500lbs. of coal per hour, height of chimney 150 feet; for 1000lbs., 100 feet and so on. The rule is of course empirical, but more reliable than any other I have tried.

The more important conclusions to be drawn from what has been said are:—

A flame-flued boiler gives its highest duty and efficiency when the firegrates are not more than twice the area of the outlet for the products of combustion at the ends of the furnace flues.

A furnace 20 square feet fed with coal and air in the proportion of 1 to 18 will radiate twice as much heat per unit of time as a furnace of 30 square feet fed with coal and air in the proportion of 1 to 30.

In our water and food supplies, the greatest care is taken to keep them pure, and still the senses of sight and smell assist us in rejecting anything impure; but the atmosphere by which we are surrounded we are compelled to breathe, no matter what impurities it contains, and to minimise air pollution, we consider a Smoke Inspector all that is necessary, and yet we have the highest medical authorities asserting dust-laden air is one of the chief causes of lung diseases.

A boiler-house arranged and worked on the lines indicated and fitted with a water meter enables the engineer to submit a weekly report to the management, giving the weight of coal burned and water evaporated, and any material change in the evaporation per pound of coal week by week gives proof of either careless stoking, defective brickwork, or inferior fuel, any of which can be attended to at once.

A boiler is giving the best results which has the greatest difference between its initial and terminal temperature.

A chimney draught costs approximately 20 per cent of the coal used in the boiler. Induced draught costs 2 per cent of the steam generated to drive the fan.

If a furnace temperature falls below 1200°, black smoke will be formed, and as each cubic foot contains 2 grains of coal, and by allowing 30lbs. of air (390 cubic feet) per lb. of coal, 11 per cent of the coal is being wasted during a black smoke period.

This brief outline does not by any means exhaust the subject of coal economy, but merely indicates some of the chief causes of wastage, and no suggestions have been submitted the writer has not had practical experience with, and his chief object is to create a national interest in this long neglected branch of engineering, and it is one of the first the Reconstructions Board should give their attention to.

In conclusion, we have in all our cities and towns, technical colleges and schools where the local staple industries are taught, all such industries are dependent on coal, when it is dear as at present, everything else follows its lead and still important as coal is, where is the technical school, college, or university where combustion and the handling of steam boilers is seriously taught? Is it not the subject of sufficient importance in Bradford alone to warrant special teachers dealing with it? The gain to Bradford would be the saving of about 130,000 tons of coal per year, and to the whole country not far short of 50 million tons.

REPORT FOR THE YEAR 1919
OF THE
FOOD INVESTIGATION BOARD DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

(Continued from p. 214.)

EXPERIMENTS have been conducted with frozen strawberries and the results have shown that, with a considerable difference between varieties, strawberries held in a frozen condition for several months appear to be quite suitable for jam-making. The acidity increases in the frozen fruit, and from the point of view of jam-making this is an advantage.

The experimental storage of plums, pears, and apples, at low temperatures and in various gases has been continued.

The results so far obtained with ordinary storage of plums at low temperatures have shown that plums picked unripe and cold stored do not ripen when subsequently brought up to normal temperatures.

The gas storage tests with plums have not yet been completed for the year under review, but in the main the results promise to be similar to those obtained with strawberries, with the addition that the ripening of plums is almost completely inhibited in nitrogen. This fruit has been found to tolerate for a considerable period an almost complete absence of oxygen without being killed or developing an alcoholic or unpleasant flavour.

Large scale gas storage tests with a number of varieties of apples and pears are in progress.

The research into the respiratory metabolism of apples, pears, plums, &c., at low temperatures has also been continued. A suitable apparatus for obtaining simultaneous measurements of a carbon dioxide production and oxygen consumption of fruits and vegetables at various temperatures and in various concentrations of oxygen has been devised and is now in use.

The investigation of the oxidising enzymes which are responsible for the discolouration or injury exhibited by some fruits has been continued at the Biochemical Laboratory, Cambridge, by the Hon. Mrs. Onslow, and some of the results have already been published. The conclusions so far reached are that in cases where the fruit turns

brown or discolours on injury an oxidising enzyme is present together with a special aromatic substance. On injury to the tissues of the fruit the enzyme oxidises the aromatic substance with the production of a brown colour. It has been found possible to group fruit provisionally into classes with regard to this phenomenon:

- (1) Fruits which discolour on injury:—these contain (as first demonstrated on the pear) an enzyme and an aromatic substance which the enzyme oxidises. In this class may be placed fruit of species of *Prunus*, e.g. the cherry, the plum, and the greengage; species of *Pyrus*, e.g. the apple and the pear, also the banana.
- (2) Fruits which do not discolour on injury:—this may be due to the following causes:—
 - (a) the presence of some inhibiting substance (probably vegetable acid) which prevents the inter-action of enzyme and aromatic substance. In this class may be placed the gooseberry and the red currant.
 - (b) the absence of the aromatic substance. This is the case in the fruits of the genus *Citrus*, e.g. the lemon, the lime, and the orange. The raspberry is also without aromatic substance.
 - (c) the absence of enzyme. This is the case in the black currant and the strawberry.

Side by side with this work Mrs. Onslow has also investigated the cause of the loss of colour in bottled fruits. The colour of fruit is known to be due to a group of red and purple colouring matters—the anthocyan pigments. These are very soluble in water even when large quantities of cane sugar, glucose, dextrin, and other substances are also dissolved. When, in heating for sterilisation, the fruit tissues are killed, the pigments dissolve out into the watery preserving medium. In solution the pigments undergo a further change (isomerisation) in which they either decolorise largely or become quite colourless. This change is prevented to some extent by acid.

Various fruits have been bottled in different media. The fruits used were blackberries, cherries, currants (black and red), gooseberries, plums, raspberries and strawberries.

Several methods of bottling were employed—

- (1) The fruits were bottled in water or solutions of cane sugar (10 per cent, 25 per cent, and 50 per cent). In some cases 1 per cent citric or tartaric acid was added. The bottles were heated to 65°–70° C. for fifteen minutes and then corked.

The pigment dissolved out, more or less, from the fruit in all cases. Black currants do not present much difficulty as they are so heavily pigmented. There was less loss of colour in the solution on the whole if sugar were employed. Acid also helped to retain the colour in cherries and strawberries and to keep the bottling fluid clear.

- (2) The fruits were bottled as in (1), but, before bottling, they were placed in a solution of formalin (1 cc. of commercial formalin to 1 litre of water) for from two to six hours. The fruit was next washed

with water. On then bottling as in (1) the pigment was largely retained in the fruit, but it becomes deeper and more purple in colour. This method only affected, to any extent, raspberries, gooseberries, and strawberries. Raspberries and some varieties of strawberries became too purple. The result with some deep-coloured varieties of strawberries and also red gooseberries was satisfactory.

- (3) The fruits were bottled in cold water without heat. The success of this method is said to be based on the absence of all air (G. Bertrand, "Sur les conserves de fruit préparées à froid sans addition de sucre, d'alcool ni d'antiseptique," *Comp. Rend.*, 1919, clxviii., 1162-4, 1285-9). The fruits were placed in bottles which were filled up with formalin solution as in (2) for from two to six hours. The fruit was next rinsed with cold water (previously boiled) and evacuated for from ten to thirty minutes or longer with a pump. The stoppers were inserted under water and sealed. Blackberries, cherries, currants (black and red), plums, and raspberries were tried, but only on a small scale. The colour was well retained, and it appeared probable that the method might be adopted with success.

In addition to the above, various methods have been tried, *e.g.*, bottling in gels of gelatine and agar (with and without boric acid) and in salicylic acid; in syrups of dextrin, sugar, &c., treatment with tannin, &c., but without success.

At the Botanical Laboratory of the Imperial College of Science and Technology, Miss D. Haynes and Miss H. Judd have nearly completed a study of the comparative changes in the sap of apples stored under normal conditions and at low temperatures. In addition, an investigation of the sampling error involved in such work has been undertaken so as to determine the limit of the observed differences between the saps, which is significant. It has been shown that the error is considerable, so that only comparatively large differences are significant unless the number of samples taken is very high.

(To be continued).

PROCEEDINGS OF SOCIETIES.

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

October 19, 1920.

(Concluded from p. 226.)

Coke Ovens.

THE next most general form of heat treatment of coal is in coke ovens. In early days the coal was treated in bulk in what is termed beehive ovens. The only product of these ovens was coke, the gaseous and liquid products of distillation being destroyed in the process. As there is no true

recovery of tar oils from this process, we can pass on to the by-product recovery oven.

The form of these ovens and the method of working will be well known to you. The principal product is coke, made for a specific purpose. About 50 per cent of the gas made is used for heating the ovens, the other 50 per cent is available for other purposes. The tar oils obtained are very similar to those made in ordinary gas works practice. An extra amount of light oil is procured by stripping the gas of its saturated hydro-carbons.

Coke ovens fulfil a definite demand for a specific article, namely, hard coke for blast furnace working. The erection of coke ovens for the heat treatment of coal to give a supply of gas and tar oils to meet national needs is not practical. The hard coke is not a commercial product except for blast furnace and foundry purposes. It is not a satisfactory fuel for producers, and therefore the cycle of coal to the coke oven and coke to the producer and a mixed gas and tar oils to the community, is not attractive.

Undoubtedly there are big developments ahead for coke ovens. The surplus gas will be utilised and should certainly be supplied in bulk to the nearest gas undertaking for distribution or to any neighbouring industrial concern requiring heat units. But improvements in working must be adopted, which will ensure an even quality of gas for distribution. At present the quality of gas from coke ovens varies too much. My personal belief is, that in the future gas, not coke, will be used to smelt iron ore. If this is so, coke ovens will be eliminated.

Gas Producers.

For many industrial purposes, such as steel manufacture, it is essential to have a large supply of heat units in the form of gas at a low cost. For this purpose, solid fuel is gasified in producers and a poor gas of about 110 to 130 B.T.U.'s obtained. Many types of gas producers will be well known to you. The great advantage of producers is that the capital cost is low, poor fuels can be used and high returns obtained by the recovery of the ammonia formed by the action of the steam in the producers on the nitrogen in the coal. I have never met anyone yet who really liked his producer plant. They fulfil a definite purpose, but they have moods. The great drawbacks to producer working, to my mind, are that the tar oils recovered are not valuable. The condition in which they come from the plant makes them difficult to work up and tar distillers tell me that the final products do not compare at all favourably in value with the final products from other methods of destructive distillation of coal.

Now that all fuel has gone up in price, and low grade fuels have risen in far greater measure than the higher grades, the economical advantages of the gas producer are not so pronounced.

Low Temperature Carbonisation.

For many years we have heard the cry against smoke in our cities. First, the deleterious effect of smoke on the human organism, vegetation and building; then the great waste of allowing all the valuable by-products of coal to go up our chimneys and be lost when they could be retained and used for the benefit of the Nation. A very proper cry! A very sound cry, and also a cry that has extracted millions of pounds from the pockets of

the public! Low temperature carbonisation should on the face of it be a simple process. Many of the difficulties of high temperature working are absent, but other difficulties crop up and to such an extent that even after the tremendous amount of fine work that has been done and the enormous sums of money that have been expended, there is not one large commercial plant in successful operation to-day in this country.

Too much has been expected of low temperature carbonisation. The advantages are too obvious. It has been too easy to draft glowing prospectuses. The problem in reality is a most difficult one. Coal is difficult stuff to handle at any time. It is as variable in behaviour as woman, and will go its own way whatever pains you may take and however conciliatory you may be in your methods.

Caking coal at low temperatures swells and sticks. The solid residue is friable, and it is very difficult to get this sticky, friable mass to leave the vessel in which it is made. Many sincere attempts have been made to solve the problem. I do not believe it to be insoluble and for my purpose I propose to take it that a process is working satisfactorily.

The tar oils obtained are high in quantity and quality. The oils are in the best form for further utilisation and treatment. I believe that with such oils processes for further cracking will become as important in the tar oil as they are in the mineral oil industry. The gas contains considerable quantities of saturated hydrocarbons, which naturally are extracted and form a very valuable supply of light fuel oils. There is the resultant solid fuel. This at present is difficult to handle owing to its friability. Improved methods of manufacture will probably give a better commercial product. It will also be found possible to satisfactorily briquet this residue.

My objection is that we still have a solid fuel with the inherent disabilities set out earlier in this paper. Producers would satisfactorily convert this fuel into gas with the recovery of ammonia and this mixed gas would be distributed for industrial and domestic use.

Total Gasification Plants.

Immediately after the commencement of the War, I heard of a plant at work in Cologne which gasified the whole of the constituents of the coal, with the exception of the ash. Since the War, I have heard that the plant was not a success. In this country we have done better and a few plants which give only gas as a product are working here, whilst a large number of these plants are being erected.

The principle of this process is the partial carbonisation of coal in a vertical retort superimposed on a water gas generator, the retort being heated externally by means of the products of combustion of the producer during the blow period and internally by the passing of the water gas made, up through the charge in the retort. The plants are built in duplicate and the gaseous products are passed up one plant and down through the other for the purpose of "fixing" all hydrocarbons and retaining them as gas. It will be readily seen that a good total heat economy should be obtained and a large make of gas given on a small area, at a low capital cost, and with a minimum of labour. There are numerous difficulties to be overcome in

order to obtain a plant which will gasify any kind of coal, not the least of which is the removal of clinker from the water gas generator and the proper and even regulation of feed and flow of coal to and through the retorts above the producer. This process gives no tar oil and to my mind this is the great detraction to its national value. Another objection is that in "fixing" the gas the ammonia as well as the tar is destroyed.

The value of this form of plant to a small gas works or as an adjunct to a large gas works can be readily appreciated. The small gas manager would only have gas to sell, no coke, no tar to store, no sulphate of ammonia manufacture to superintend. In a large gas works the production of coke could be regulated to meet the market and a plant capable of producing large quantities of gas at a low capital cost with a minimum of labour would be available.

The Ideal System.

After having thus very briefly reviewed the various processes for the heat treatment of coal, I venture to formulate a system of manufacture to meet the demand for liquid and gaseous fuels for practically all purposes. The total gasification of coal is essential, preferably in one vessel. The plant must be economical in first cost, and low in labour charges, but above all the maximum amount of the volatiles in the coal must be recovered in a liquid form, being distilled over at such temperatures and in such a manner that a minimum of cracking takes place. The gas afterwards should be stripped of all saturated hydrocarbons and supplied to the consumer constant in heat value and specific gravity.

Further, special care must be taken to preserve the ammonia obtained from the nitrogen in the coal. The plant must be designed to work with any coal, but I do believe it possible to design a plant of this type capable of working greatly varying coals over short periods, or of working coal containing, say, over 60 to 70 per cent of fines.

The form of plant I would suggest is one or more vertical retorts superimposed over a water gas producer, the retorts being so constructed and heated that even difficult coals like Durham will work through without undue attention, and the coal fully converted into coke before entering the producer. The producer should be built and worked to obviate the formation of hard clinker, with mechanical grates for the continuous and clean removal of the ash. Automatic compensating devices would have to be included for the regulation of the pressure in the retorts during the run and blow periods. Such a plant, fitted with recuperators and waste heat boilers, would have a very efficient heat cycle, which would undoubtedly result in a large conservation of fuel. If the major portion of the coal used in this country were first treated by such a process, the fuel oil position would be made much easier, as greatly increased supplies would be forthcoming, the demand would accordingly greatly increase, and, as far as I can calculate, gas could be distributed to consumers at from one-and-a-half times to twice the amount it would cost per heat unit to supply as solid fuel. The saving in labour and transport, the cleanliness, and the efficiency of utilisation would far more than compensate for this increased charge.

CORRESPONDENCE.

RELATIVITY.*

To the Editor of the Chemical News.

SIR,—A study of the above work has led me to the conclusion that the whole theory is based upon a fundamental error.

In discussing "the idea of time in physics" in Section VIII., Dr. Einstein confuses the time when an occurrence took place with the time when the record reached an observer, or recording instrument, and his test of the simultaneity of the two lightning flashes, taken as examples, is only accurate when the component of the motion of the railway embankment through the aether from the flashes towards the observer is zero.

When due account of these factors is taken, it appears to me that what follows about the difference of time recorded for the flashes as observed on the bank and on the moving train is simply a record of the speed of the train relative to the embankment, and there is no need to assume anything about the different rates of clocks when at rest and when in motion, or of the shortening of matter in the direction of its motion. Rather may it be predicted that when measurements of length, speed, and time are made with the requisite precision, no such phenomena will be found to occur other than are due to well known physical causes.

It must not be forgotten that Dr. Einstein predicted that in accordance with his theory it would be found that rays of light passing near the sun would be bent; and to test this, a photograph of the sun during an eclipse was taken in May, 1919, and the positions of several stars adjacent compared with their positions as shown in another photograph of these stars when the sun was elsewhere. The result of the comparison was that the stars selected all showed a displacement of about the expected amount, and in the required direction. This has been taken to be a complete confirmation of the theory.

In my opinion it all depends on whether the displacement of the star images took place during exposure of the plate, or subsequently during development and fixing.

That the latter can occur in the case of photographs of spectra of the elements was suspected, tested, and proved, but never published, by my father, the late Sir William Crookes.

The test was made in the following manner: A negative, with two spectra, slightly overlapping, was selected, which had at one part of it a group of strong lines, and at another part few and weak lines. From this negative a contact positive was printed, and from the positive another contact negative. The two negatives were then measured in the usual manner, along the overlap of the two spectra, and compared, and the following results noted; (a) the whole negative altered in length; (b) the alteration took place in a "concertina" fashion, being greater where the lines were strong and numerous than where they were light and few; (c) one or two lines showed decided displacement with regard to their neighbours in the same spectrum. The conclusion drawn was that during development and fixing the sensitive film was in

a state of tension, and yielded to the strain irregularly in proportion to the depth and width it had been altered by the light rays. It would then seem that the spectra had been measured along the very worst line, where distortion would be greatest, and arrangements were being made to alter the shuttering of the spectroscope so that the measurements could be taken along a line only just off the unexposed part of the plate, where distortion would be least, but death intervened, and the alteration was never made. Applying the information gleaned from the above-described experiment to stellar photographs, it would appear that in general there is no line of weakness in them, but in an eclipse of the sun the ring of flames would form a very decided line of weakness, and it is worth considering whether the displacement of the star images is not really due to the sensitive film yielding to strain in this neighbourhood during development and fixing; and if this be so, a similar effect should be found during an annular eclipse of the moon, and it is possible that a careful examination might disclose a slight displacement during a close conjunction of a star with Jupiter or Venus when at their brightest. Bright star clusters also might show systematic divergencies between the photographic and visual positions. In view of the scientific problem involved, such an examination appears desirable.—I am, &c.,

B. H. CROOKES.

QUINOLINE FROM ANILINE STANNICHLORIDE.

To the Editor of the Chemical News.

SIR,—In his article on "A Modification of Skraup's Quinoline Synthesis," Mr. Edward de Barry Barnett makes reference, in your issue of October 29, to a paper of mine (CHEMICAL NEWS, 1918, cxvii., 346) describing a method of preparing quinoline from aniline stannichloride.

He finds it difficult to understand the production of 20 grms. of quinoline from 50 grms. of aniline stannichloride, as this is 161 per cent of that theoretically possible, calculated on the tetravalent tin present, although 80 per cent of the theoretical quantity, calculated on the aniline.

The results are not so difficult to understand when it is remembered, as Mr. Barnett mentions later (p. 206), that stannous sulphate is easily oxidised to the stannic salt.

The tin alone may not account for all the oxidation which takes place. It is quite possible that the concentrated sulphuric acid employed may be responsible for some oxidation.

The nitrobenzene used in the older methods of preparation (yielding 50-75 per cent quinoline calculated on the aniline) is not generally used as a basis of calculating the percentage yield, since the exact mechanism of the oxidation is, so far as I am aware, obscure.

Mr. Barnett also suggests it is superfluous to use the stannichloride, but the hydrogen chloride liberated when it is employed appeared to me to have a favourable effect upon the reaction, which takes place quite smoothly. That this is so receives support from Mr. Barnett's observation that stannic sulphate did not give such good results.—I am, &c.,

J. G. F. DRUCE, M.Sc. (Lond.), A.I.C.

The Chemical Laboratory,
Battersea Grammar School, S.W.11.

*"Relativity: The Special and the General Theory. A popular Exposition." By A. Einstein. Translated by Robert W. Lawson, D.Sc.

INSTITUTION OF ELECTRICAL ENGINEERS.—The Opening Meeting of the Session has been postponed to Thursday, November 18, when the meeting will be held at the Institution of Civil Engineers, at 6 p.m., and the President, Mr. L. B. Atkinson, will deliver his Inaugural Address. The Wireless Sectional Meeting announced for November 17 has been postponed to November 24 (at the Institution of Civil Engineers, at 6 p.m.).

MEETINGS FOR THE WEEK.

Wednesday, November 17.

Royal Society of Arts, 8. "Wireless Telegraphy and Telephony" by Alan A. Campbell Swinton, F.R.S.
Society of Glass Technology, 3. (At Leeds).

Thursday, November 18.

Royal Society, 4.30. "Absorption and Scattering of Light" by Sir Arthur Schuster.
"The Emission of Electrons under the Influence of Chemical Action" by Prof. O. W. Richardson.
"Magnetism and Atomic Structure" by A. E. Oxley, D.Sc.
"Proximity of Atoms in Gaseous Molecules" by Prof. A. O. Rankine.
"Similarity between Carbon Dioxide and Nitrous Oxide" by Prof. A. O. Rankine.
"Forces in Surface Films" by A. M. Williams, D.Sc.

NOTICES.

EDITORIAL.—All literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the Editor.

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A MEETING of the Research Fund Committee will be held in December next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, Chemical Society, Burlington House, W.1., must be received on or before Monday, December 6th, 1920.

All persons who received grants in December, 1920, or in December of any previous year, whose accounts have not been declared closed by the Council are reminded that reports must be returned by Wednesday December 1st, 1920.

CITY OF BIRMINGHAM.

A JUNIOR MALE ASSISTANT (A.I.C. or B.Sc.) is required in the CITY ANALYST'S LABORATORY, at a basic salary of £150, which with the new Civil Service bonus makes the total salary at present about £380 per annum. Payments have to be made to the Birmingham Superannuation Fund.

Applications, stating age and qualifications, accompanied by not more than three testimonials, to be addressed to the City Analyst 4, Broad Street, Birmingham.

BRADFORD EDUCATION COMMITTEE TECHNICAL COLLEGE. LECTURER IN DYEING.

APPLICATIONS are invited for a Lectureship in Dyeing in the College. A Salary up to £450 per annum will be paid to a candidate of suitable qualifications and experience. In addition to the salary a bonus of £85 18s. per annum is at present paid.

Applications, upon forms which may be obtained from the Principal, should be forwarded not later than 15th December.

BY ORDER.

5th November, 1920.

TO STEAM USERS. FOR SALE.

A QUANTITY of second-hand light rivetted steel piping 18in. dia., suitable for small factory chimneys, together with cast iron tees and bends; also a number of 4in., 5in., 6in. and 7in. water and steam valves of Hopkinson's make; various lengths of 6in. steel and cast iron piping; tees; bends, and other material. For further particulars apply to the Engineer and Manager, 27, Osborn Street, Whitechapel, London, E.1.

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DEPARTMENT OF COLOUR CHEMISTRY AND DYEING.

THE COUNCIL will shortly proceed to the appointment of a Lecturer and Research Chemist in Colour Chemistry and Dyeing, at a salary of £550 a year. Preference will be given to a candidate with some works experience. Applications should be addressed to THE SECRETARY, The University, Leeds, from whom further particulars may be obtained.

CHEMIST with Metallurgical or Analytical experience or having experience in heavy Chemical Works wanted. Age 25-35. Single preferred. Write, stating age, salary required, past experience to:

QUIMICOS, c/o Streets,
30, Cornhill,
E.C.3.

YOUNG MAN as Junior Assistant in Chemical Laboratory at Messina, Sicily. About 21 years of age. Quick and accurate worker required. Write particulars of qualifications to M., c/o Ogston & Moore, 87/9, Aldgate, E.1.

PATENTS, TRADE MARKS. Handbook and advice free—B. T. KING, British and U. S. Regd. Patent Attorney, 146a, Queen Victoria St., London. 35 years reference

If in good condition, Sixpence per copy will be paid for any of the undermentioned numbers of the CHEMICAL NEWS which may be forwarded to this office:—

3048, May 24th, 1918.
3051, July 5th, 1918.
3053, August 2nd, 1918.
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3056, September 13th, 1918.
3059, October 25th, 1918.
3062, December 6th, 1918.
3063, December 20th, 1918.
3064, January 3rd, 1919.
3066, January 17th, 1919.
3068, January 31st, 1919.
3069, February 7th, 1919.
3070, February 14th, 1919.
3075, March 21st, 1919.

CHEMICAL NEWS OFFICE, 97, SHOE LANE, LONDON, E.C.4

THE CHEMICAL NEWS.

VOL. CXXI., No. 3162.

EDITORIAL.

THE following paper has been received:—

"RELATIVITY: A FEW SELECTIONS FROM RECENT LITERATURE." By F. H. LORING. Received November 1, 1920. A collection of quotations and abstracts from current literature upon this subject.

THE PHYSICS AND CHEMISTRY OF COLLOIDS AND THEIR BEARING ON INDUSTRIAL QUESTIONS.*

THE PROPERTIES OF ELASTIC GELS.

By EMIL HATSCHKE, F.Inst.P.

THE statement that the familiar table jellies (gelatin gel) are typical representatives of the class to be discussed in the present paper will probably, at the outset, be found more useful than an attempt at strict definition. These systems exhibit immediately two of the most characteristic properties of the elastic gel: stability of shape, notwithstanding a very high content of liquid (about 95 per cent in the case quoted) and perfect elasticity within certain narrow limits.

The gel may be obtained in two opposite ways: either by transformation—which may be reversible or irreversible—of a sol, e.g., by cooling a gelatin sol below a certain temperature; or by allowing the dry substance to "swell" in an appropriate liquid. Practically all substances from which elastic gels may be produced show this capacity of swelling, though to an extent which differs widely. Only certain liquids will cause a given substance to swell, and the relations between the constitution of the solid and the liquid, on which this property is based, are at present quite obscure. Thus gelatin and agar (the former a protein, the latter a mixture of carbohydrates) swell in water at ordinary temperature, but do not dissolve until the temperature is raised. Vulcanised india-rubber swells in various organic solvents such as benzene, toluene, or xylene, without dissolving. Finally, the processes of swelling and dispersion or solution may proceed *pari passu*, as with gum arabic at ordinary temperature. At low temperature, a definite stage of swelling may be observed to precede solution.

The elastic gel which can be most easily reproduced and has, accordingly, been studied most frequently and extensively, is that of gelatin. Bodies of any desired shape can be obtained by pouring the gelatin sol into suitable moulds and allowing it to set for a period of not less than 24 hours (*cf. infra*, E. Fraas). The procedure, once chosen, must be rigidly adhered to throughout, since all the properties of a gel depend, not only

on its composition, but also to a marked extent on its history, especially its "thermal history," i.e., the temperatures to which the sol has been exposed and the duration of such exposure. Some of the principal investigations will now be briefly summarised.

Elastic Properties.

These have been studied principally by R. Maurer (R. Maurer, *Ann. d. Phys.*, 1866, xxviii., 628), P. v. Bjerken (P. v. Bjerken, *ibid.*, 1891, xliii., 917), E. Fraas (E. Fraas, *ibid.*, 1894, liii., 1074), and A. Leick (A. Leick, *ibid.*, (Drude), 1904, xiv., 139). All these investigations date back some time, and were undertaken with a view to studying a material with very low modulus and sufficiently transparent for examination in polarised light, rather than with the intention of elucidating such problems as the structure of gels. Both Maurer and Leick determined Poisson's ratio for gels of various concentrations and find it 0.5 within the limits of error—a result which is not surprising in view of the large percentage of liquid. Maurer studied the elongation of gel cylinders of considerable diameter (2.21 cm.) with small loads, the extensions being measured microscopically. His figures for the modulus are in good agreement with those found by Leick, which range from 2.42 (grm./mm²) for 10 per cent to 20.4 for 45 per cent gels. Leick found the modulus E roughly proportional to the square of the gelatin concentration; the ratio E/c², however, varies somewhat irregularly, and decreases with increasing c. All the investigators find that the modulus increases with increasing load.

Fraas studied the ageing of gels and found that a constant modulus was not reached until about 24 hours after apparently complete setting. These hysteresis effects are universal in colloidal systems, and the increasing modulus of a gel is paralleled by the increasing viscosity of the sol, when kept at a temperature above the setting point. In the following table one series of Fraas's results is given to illustrate the magnitude of the effect.

Cylinder of 20 per cent Gelatin Gel.

Hours after removal from mould ...	1	2	3	4	5	6	7	24
Extension produced by 50 grms. weight	12.5	7.5	7	7	6.5	6.5	6	5

Maurer, and more particularly Leick, also studied the effect of various substances dissolved in the water on the elastic modulus of gelatin gels; the results are of particular interest from the colloidal point of view, inasmuch as they can be co-ordinated with the well-known effects of such solutes on other properties of the system, e.g., maximum swelling, setting point of sol, &c. Leick finds that the addition of various chlorides lowers the modulus, sodium sulphate is without action, while cane sugar and glycerine raise the modulus considerably. Chlorides also lower the viscosity and setting temperature of the sol, while glycerine and cane sugar (generally substances containing hydroxyl groups) raise both constants.

The elasticity of gels is perfect only for small loads applied for a short time, but very little work has been done on relaxation in such systems. R. O. Rankine (R. O. Rankine, *Phil. Mag. A.*,

* A General Discussion before the Faraday Society and the Physical Society of London, October 25, 1920.

1906, 447) maintained gelatin gels of low concentrations (3.4 to 4.5 per cent) at constant strain and plotted the stress necessary to do this against time. The stress, within the limits of concentration and time investigated, never becomes zero. Breaks occur in the time-stress curves, which are taken to indicate that the elastic limit has been reached. The concentrations employed by Rankine are very much lower than those at which determinations of the modulus, &c. have been made.

Reiger (R. Reiger, *Phys. Zeitschr.*, 1901, ii, 213) determined the relaxation time of gelatin gels by optical means (disappearance of the double refraction produced by strain). The investigation was undertaken with the object of testing Maxwell's relation between modulus, viscosity and relaxation time, and was accordingly carried out at 29° C., i.e., at a temperature very near the "melting point" of the gel. In these conditions Reiger found a relaxation time of 10 minutes for 20 per cent, and about 41 minutes for 40 per cent gel.

That the conditions are entirely different at lower temperatures is shown by experiments by the writer, published here for the first time. Rectangular prisms of gelatin gel (10 per cent) with 1 per cent of sodium fluoride, to prevent putrefaction, were cast and allowed to set for 36 hours before removal from the mould. One of these prisms was then bent between three stops fixed on a glass plate, the latter being covered with paraffin oil to prevent adhesion of the gel and consequent irregular deformation. The specimen was then photographed in polarised light (double plate glass as polariser, Nicol as analyser) within 10 minutes of the application of stress at room temperature, about 15° C. The glass plate with the specimen was then placed in a moist chamber for five days, being examined at intervals (visually) without any noticeable change showing itself. At the end of five days the stress had practically disappeared, so that the specimen could be removed without friction and without straightening itself appreciably. It was then again placed on an oiled glass plate and photographed as before. Considering the extreme sensitiveness of 10 per cent gel to deformation, it may be said that the appearance is substantially unaltered, and that at any rate the optical anisotropy caused by strain has not disappeared with the removal of the stress. The absence of relaxation in a system consisting to about 90 per cent of liquid is certainly remarkable and will be referred to again.

Optical Properties.

The double refraction produced by deformation has been referred to incidentally in the preceding paragraph. Quantitative investigation of this property has been carried out chiefly by Leick (*l.c.*). His principal results (obtained with gel plates in tension) are: (1) the double refraction ($D = n_e - n_o$) is, *ceteris paribus*, very approximately proportional to the strain, and (2) for equal relative elongations the double refraction is roughly proportional to the gelatin content.

The refractive index of both gelatin sols and gels has been shown by G. S. Walpole to be a linear function of the gelatin concentration G. S. Walpole, *Koll. Zeitschr.*, 1913, xiii, 241). If the

refractive index is plotted against the temperature over a range containing the setting point, no discontinuity occurs at the latter, i.e., when the sol is transformed into gel.

On the whole, our knowledge of the elastic and the related optical properties of gels must be pronounced slight. As in other branches of the subject, non-aqueous systems have received hardly any attention; their study is eminently desirable, as the enormous complications introduced in the case of a protein like gelatin by the formation of salts, and their electrolytic and hydrolytic dissociation, would be absent. There is a very large literature on the stress-elongation curve of india-rubber, which, however, refers only to the dry material and is not of immediate interest. The writer has found only one reference to a rubber gel in a paper by A. E. Lundal (A. E. Lundal, *Ann. d. Phys.*, 1898, lxvi, 741), who determined the tensile modulus of rubber which had imbibed 133 per cent of paraffin oil and found it about one-half that of the dry material.

Diffusion in Gels.

This phenomenon has, for various obvious reasons, received a considerable amount of attention. Thos. Graham already used dilute gels instead of pure aqueous solutions in the study of diffusion, and found the rate approximately the same in both. This, however, only holds good of gelatin gels up to, say, 3 or 4 per cent and agar gels under 1 per cent. In more concentrated gels the rate of diffusion decreases markedly with the concentration, but no quantitative relations have, so far, been determined. The rate of diffusion for a given solution and gel concentration can be affected by various solutes in the latter. Among the earliest investigations on the point are those of H. Bechhold and J. Ziegler (H. Bechhold and J. Ziegler, *Zeitschr. phys. Chem.*, 1906, lvi, 105), who found NaCl and NaI without effect; Na_2SO_4 and several non-electrolytes as dextrose, glycerin and alcohol reduced the rate of diffusion of certain solutes. A certain—though not exact—parallelism shows itself between the effect of solutes on the elastic modulus and the rate of diffusion: substances which increase the former reduce the latter. The experimental difficulties are very considerable and are explained in the literature. Among more recent papers on the subject are those by O. v. Fürth and F. Bubanovic (O. v. Fürth and F. Bubanovic, *Biochem. Zeitschr.*, 1918, xc., 265; xcii., 139), and by W. Stiles (W. Stiles, *Biochem. J.*, 1920, xiv., 58).

The fact that both the swelling and the drying of gels are controlled by diffusion involves some consequences which, considering that they may have an important bearing on histology and related subjects, have not yet received adequate attention. If a body of a gel is bounded by a surface in which the radius of curvature changes very quickly or (as in polyhedra cylinders bounded by plane ends, &c.) discontinuously, diffusion to or from regions adjacent to tracts of surface with low or zero-radius takes place more rapidly than from the rest. The result is that a body of gel does not remain similar to itself during swelling or drying, but undergoes successive deformations which may be considerable. The effect is particularly marked in drying; thus, cylinders with plane ends at first dry more rapidly

round the circular edges, which contract, the profile becoming that of a barrel with convex ends. As the material forming the edges becomes less permeable, the large surfaces dry more quickly, and the final shape is, approximately, a single-shell hyperboloid with concave ends. On allowing such a body of dry gel to swell again, the original shape is not necessarily restored; the reason for this alteration in the capacity of absorbing water is obscure (E. B. Shreve, *Science*, 1918, xlviii., 324; *Jl. Frank. Inst.*, clxxxvii., 319).

The foregoing summary—though necessarily restricted by considerations of space—may give the reader unfamiliar with the literature some idea of our present knowledge. The two great problems to be solved must now be set forth briefly. They are (1) the elucidation of the structure of elastic gels, and (2) the explanation of the phenomenon of swelling. As regards the former, there is at present a fundamental divergence of opinion, inasmuch as some authors (H. Procter, W. Pauli, and J. R. Katz) maintain that elastic gels are *homogeneous* systems, i.e., solid or (H. Procter) "semi-solid" solutions. The evidence for this view is set forth at length in a very exhaustive monograph by Katz (J. R. Katz, *die Gesetze der Quellung, Koll. Reib.*, 1917, ix.). The other school (W. B. Hardy, W. Ostwald, W. Ostwald, S. C. Bradford, Dorothy J. Lloyd) consider gels to be heterogeneous systems, but differ regarding the state of aggregation of the phases. Ostwald, in particular, considers gels to be *systems of two liquid phases* having an interfacial tension, while some of the other investigators incline to the view that the properties of gels are best accounted for by assuming some sort of network or cellular arrangement of *solid* phase permeated by liquid. Speaking generally, these rival theories are based on the consideration of a limited number of selected properties, and a great deal of further work is required, probably on quite novel lines, before a definite conclusion commanding universal acceptance can be reached. The author feels, in particular, that the elastic properties have received insufficient attention, and has attempted, as a first step, to examine whether they are compatible with the assumption of two liquid phases possessing interfacial tension (E. Hatschek, *Trans. Faraday Soc.*, 1916, xii., Part 1), the result being negative if the assumptions necessary to allow of mathematical treatment are granted.

As regards the phenomenon of swelling, we have at present no explanation whatever why certain substances swell in a comparatively limited number of liquids. In the case of proteins, which have received the greatest attention, conditions are enormously complicated through salt formation and electrolytic and hydrolytic dissociation, and here, as in other problems of colloid chemistry, substantial progress is to be expected only from the study of non-aqueous systems, of which a large number is certainly available. This is also the view expressed by Katz in the monograph already quoted: "Swelling in organic solvents would, perhaps, be more important for an investigation in the service of pure physical chemistry than swelling in water." It is greatly to be hoped that the present discussion may induce competent workers to examine this—equally neglected and promising—field.

THE CONSTITUTION AND STRUCTURE OF THE RADIO-ACTIVE ELEMENTS.

By HAWKSWORTH COLLINS.

ALL the deductions in preceding papers have been obtained by observing and then reasoning upon batches of concordant coincidences in numerical facts. When these facts are fairly numerous, it is possible to take into consideration all available facts and find out by the theory of mathematical probability whether the apparent coincidences are merely coincidences or whether they involve absolute truths. But when the number of facts is limited as in the case of the radio-active elements, it is not possible to employ the theory of mathematical probability, so that there is no claim that the following matter is proved to be true.

In mathematics the word "theory" is used in its original meaning of "something that is seen (to be true)"; and is not employed at all in the sense of "hypothesis" or "guesswork"; e.g., the Theory of Quadratic Equations does not contain anything of the nature of hypothesis. But in Chemistry the words "theoretical" and "hypothetical" are used synonymously, so that unfortunately a mathematical theory may be spoken of as "a piece of theoretical work" an expression which is entirely misleading. All the deductions in previous papers have been proved to be true mathematical theories, and if anyone were to speak of them as "theoretical conclusions" he would be employing an expression which has a meaning exactly opposite to that which he intends to convey.

The observation of the following coincidences with regard to numerical facts concerning radio-active elements is due to the preceding mathematical theories, so that the probability of the truth of the matter is much greater than it would be if it were an entirely independent investigation.

The main characteristic constituent of the radio-elements is a portion represented by hexadic titanium.

No one could possibly have guessed or hypothesised this and then made the facts fit into his hypothesis.

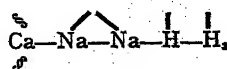
In Table I. the atomic weights of the radio-elements are split up in different ways into parts which happen to represent nearly all the characteristic elements with which they are associated in mineralogy, so that there is a very great probability that the radio-elements and their associated elements are interrelated.

TABLE I.

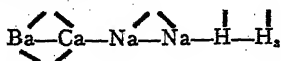
U	=	CbYFe	=	TaFe	=	338
Th	=	CbZrTi	=	CbLa	=	WTi = 332
Io	=	CbYTt	=	TaTi	=	CbBa = 230
Ra	=	ZrBa	=	ZrYTi	=	LaY = 226
where						
Cb = Na ₂ Ti						
Y = CaTi						
Ba = CaTi ₂						
La = ZrTi						

Radium = ZrBa

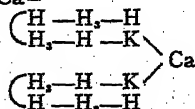
The constitution and structure of Zr has been given as



Ba must have united with it to form Ra in the following manner:—

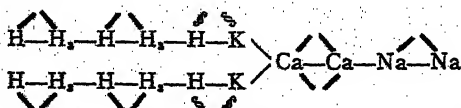


where Ba = Ti, Ca =



The doubling up of the titanium-portions is intended to signify that the helium-portions of titanium are not free to vibrate, and that the twelve valences are quiescent.

The shock to the remaining portion of Ra when H—H₂ is suddenly projected from its Zr portion must cause some atomising bonds to be broken, so that the two Ti-portions are released in the following manner, and by their vibrations cause Niton to have the nature of a very heavy gaseous emanation:—



The remaining helium-portions are then given off in turn and Pb is left:—



This is a very suitable formula, since Pb is especially connected with Ca, its ultimate matrix being limestone.

In order to demonstrate the way in which the theory accounts for the emission of the negative β -particles, the following facts must be mentioned: Al is monobasic and diacidic, *i.e.*, it has a single electro-negative valence free for combination with a base, and a pair of electro-positive valences free to combine with the two electro-negative valences of an atom of oxygen. The theory shows that if Al (=Na—H—H₂) could give off H—H₂ with its two positive charges, the single negative charge emanating from Na would be left. But since this negative charge is only due to the presence of the free H—H₂, it becomes, what it potentially is, a positive charge by throwing off the negative β -particle.

Similarly, if Si (=Na—H—H₂—H) were to throw off its helium-portion, two negative β -particles would follow of necessity. And if Ti (=K—H—H₂—H—H₂—H) were to throw off its two helium-portions one after the other, there would again be two β -particles to follow.

Consequently it may reasonably be expected that if a triadic portion (like Al) of a radio-active element were being disintegrated, a β -particle would follow the emission of a single α -particle; and if a tetradic portion (like Si) were being disintegrated, two β -particles would follow an α -particle, and if a hexadic portion (like Ti) were being disintegrated, two β -particles would follow two α -particles.

When this reasoning is considered in relation to the observed facts regarding Ra, there is no β -particle to come off (as previously shown) after the expulsion of the first atom of helium. In the structure given for Nt the twelve quiescent charges represent the twelve metastatic electrons.

If these become active, *i.e.*, become valency electrons as the disintegration proceeds, there will finally be left the four valences of Pb.

The manner in which two slightly different products of equal mass can be produced may be illustrated by the above formula for niton. If the two helium-portions were given off from one Ti-portion, they would be followed immediately by two β -particles; but if one helium-portion were given off from each of the Ti-portions, there would be no emission of β -particles until after the expulsion of a third atom of helium.

There is no doubt that the theory is in almost exact agreement with observed facts with regard to the disintegration products of radium.

Uranium = CbYFe

As iron is the main constituent of meteorites, it is probable that this element is readily formed from more elementary matter; and this probability is increased by the following facts: If helium could be given off from Fe (56) a product of the same mass as Cr (52) would be left; and if helium could be given off from the latter a product of the same mass as Ti (48) would be left; and if another helium could be thrown off, Sc (44) would be left; and if one more, then Ca (40) would remain; so that it is reasonable to expect that Fe may produce Ca by giving off four helium-portions, especially as this particular series with a difference of four begins with Ca and ends with Fe, for there are no elements of atomic weights 36 and 60.

Then since U = CbYFe, and Cb = Na₂Ti, and Y = CaTi, there are altogether eight helium-portions to come off from U (238) before Pb (206) is left, and the different order in which they may come off causes the production of isobares.

According to the theory there would be six β -particles to come off, and this is in accordance with the observed facts.

Ionium = CbYTi

According to the theory there are six helium atoms available, two from the Cb-portion, two from Y and two from Ti. There are also six β -particles to come off before Pb (206) is left.

Thorium = CbZrTi

According to the theory there are only five helium-portions available as disintegration products, leaving a mass of 212 composed of Na₂Ca from Cb, Na₂Ca from Zr, and Ca from Ti, *i.e.*, Na₂Ca, altogether. This remnant would evidently be something like lead but would not be lead. As it appears to be impossible to separate ionium and thorium chemically, the observed facts with regard to their disintegration products are probably confused; and the variable atomic weights found experimentally for the end-products of disintegrating radio-elements are probably due to mixtures of elements represented by 206 and 212.

INSTITUTION OF MINING AND METALLURGY.—The Gold Medal of the Institution of Mining and Metallurgy, the highest distinction in the power of the Council to bestow, has been awarded to Sir Thomas Kirke Rose, D.Sc., Assoc.R.S.M., M.Inst.M.M., "in recognition of his eminent services in the advancement of Metallurgical Science with special reference to the Metallurgy of Gold." "The Consolidated Gold Fields of South Africa, Ltd." Gold Medal and Premium of Forty Guineas have been awarded to Mr. H. Livingstone Sulman for his paper, "A Contribution to the Study of Flotation" (*Transactions*, 1919-1920, vol. xxix.).

DETERMINATION OF MOLYBDENUM.

By J. P. BONARDI and EDWARD P. BARRETT.

(Continued from p. 233.)

Effect of Sulphuric Acid.

IN order to determine the effect of sulphuric acid on the precipitation of molybdenum by lead acetate, the molybdenum was determined in samples taken from a solution of ammonium molybdate when no sulphuric acid was present, and in the presence of 15 cc. of concentrated sulphuric acid in samples containing amounts of molybdenum equal to those of the first samples. The concentration of the solutions and the procedure were the same as outlined in the detailed gravimetric method.

15 cc. of sulphuric acid was used because that volume represents approximately 27.60 grms. of acid, a greater weight than that of the sulphates that would be present in a sample taken for analysis, even after fuming with 10 cc. of acid.

The following table shows the results, which indicate that sulphuric acid does not interfere with the precipitation of molybdenum by lead acetate if precautions are taken as described in the details of the gravimetric method, especially as given under "Precipitation." As the solution containing molybdenum is titrated with a lead acetate solution and only 2 cc. excess is added, the amount of lead sulphate that might form would be readily soluble in the hot acetate solution.

TABLE I.—*Results of Precipitation of Pb MoO₄ with and without sulphuric acid, first series of tests.*

Sample No.	Mo present in sample	Mo by gravimetric method.			Mo by volumetric method (titration with KMnO ₄)
		Without H ₂ SO ₄	In presence of 15 c. c. of concentrated H ₂ SO ₄		
	Per cent.	Per cent.	Per cent.		Per cent.
1	6.26	6.26	6.35		6.24
2	6.26	6.27	6.36		6.24
3	6.31	6.31	6.41		6.30
4	6.31	6.31	6.38		6.30

The column of volumetric determinations is added to the table to serve as a check on the gravimetric determinations. The same standard ammonium molybdate solution was used, acidified with sulphuric acid, and then passed through the Jones reductor; the acidity of solution and the procedure were the same as given under the description of the volumetric method.

As a further test two 1-grm. and two 0.25-grm. samples of a high-grade molybdenite ore were weighed. The 1-grm. samples were decomposed with aqua regia and the molybdenum precipitated with lead acetate. The 0.25-grm. samples were decomposed with aqua regia and one was fumed with 5 cc. of concentrated sulphuric acid and the molybdenum precipitated with lead acetate. The results, given in Table II., justify the conclusion that sulphuric acid does not interfere with the precipitation of lead molybdate if this is conducted as given under "Precipitation."

TABLE II.—*Results of precipitation of PbMoO₄ with and without sulphuric acid, second series of tests.*

Sample No.	Weight.	Mo content by aqua regia decomposition—	
		Without H ₂ SO ₄	Followed by addition of 5 c.c. of concentrated H ₂ SO ₄ and boiling to fumes.
	Grms.	Per cent.	Per cent.
1	1.00	46.25	—
2	1.00	46.51	—
3	0.25	46.00	—
4	0.25	—	46.29
Average	—	46.25	46.29

No sample ever taken for analysis and decomposed by aqua regia would contain as much sulphates as is produced by 5 cc. of concentrated sulphuric acid, consequently the amount of lead sulphate formed by the small excess of lead acetate (2 cc.) added to the molybdenum solution when titrating would be rendered soluble in the acetates present. If lead sulphate should be carried down mechanically with the lead molybdate this would, under the vigorous boiling after precipitation, be rendered soluble during the change in form of the bulky lead molybdate to the granular form.

Effect of Lime.

In order to test the effect of lime on the gravimetric method two samples representing 6.31 per cent molybdenum on a 1-grm. basis were prepared. To each was added 3 grms. of precipitated calcium carbonate just acidified with hydrochloric acid. The molybdenum was then determined in the samples by the procedure given for the gravimetric method. The results, presented in Table III., show that a large excess of lime will slightly lower the percentage of molybdenum obtained.

TABLE III.—*Results of precipitation of PbMoO₄ in the presence of Lime.*

Sample No.	CaCO ₃ added. Grms.	Mo present Per cent.	Mo determined. Per cent.
1	3.00	6.31	6.09
2	3.00	6.31	6.10

However, as the 3 grms. of precipitated calcium carbonate present in these tests lowered the percentage of molybdenum only 0.21, probably the small proportion of lime present in the ordinary run of molybdenum ore does not cause any appreciable difference.

If the ore should be high in lime the molybdenum can be determined by the volumetric (KMnO₄) method, or the lime can be removed from the alkaline solution by means of sodium carbonate before precipitating the lead molybdate. Molybdenum remains in solution. Two precipitations should be made, washing the precipitate well each time.

As calcium molybdate is partly precipitated from a solution slightly acidified with acetic acid only when the solution is boiled vigorously for a prolonged period, it is essential that the directions given under "Precipitation" be followed closely.

Purity of the Precipitated Lead Molybdate.

In order to test the purity of the precipitated lead molybdate that was obtained by the gravimetric method of determination the ignited lead molybdate was weighed, dissolved, and the molybdenum redetermined by reduction in the Jones reductor and titration with potassium permanganate. Table IV. shows the results obtained.

TABLE IV.—Results of Tests of Purity of Precipitated $PbMoO_4$.

Sample No.	Mo content by—		$PbMoO_4$ dissolved, titrated with $KmnO_4$ Per cent.
	Volumetric method ($KmnO_4$) Per cent.	Gravimetric method ($PbMoO_4$) Per cent.	
1	5.580	5.550	5.510
2	1.000	2.000	1.960
3	8.530	8.390	8.310
4	6.480	6.560	6.380
5	6.740	6.910	6.690
6	5.520	5.620	5.440
7	0.941	0.875	0.890
8	0.203	0.208	0.200
9	0.425	0.439	0.440
10	0.154	0.133	0.138

The ignited lead molybdate dissolved entirely in hydrochloric acid, thus showing that the precipitate was not contaminated with silica or insoluble material. If vanadium is suspected to be present in the ore, the solution of dissolved lead molybdate can be tested for vanadium by means of hydrogen peroxide. The solution will become reddish brown if any vanadium is present, from the formation of pervanadic acid (HVO_4). This is a very delicate reaction.

Vanadium is precipitated from solution as lead vanadate in precisely the same manner as lead molybdate. The lead vanadate, however, is not weighed, but the vanadium is calculated as in the determination for molybdenum, because the composition of the precipitated lead vanadate is not always definite. The determination of vanadium and molybdenum when occurring together is described elsewhere in this paper under "Separation of Molybdenum from Vanadium."

(To be continued.)

REPORT FOR THE YEAR 1919
OF THE
FOOD INVESTIGATION BOARD DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

(Continued from p. 237.)

SOME of the main results of the preliminary chemical study of the cell saps of the apples stored under the two sets of conditions are:—(1) there is a marked disappearance of cane sugar during the earlier stages of storing; (2) the ratio of acids to sugars shows a decided fall towards the end of the period of storage; (3) there is a

sudden rise in the content of sugar and of acid in both sets of apples at about the tenth week; (4) the tissue changes which are associated with "rotting" of the apples are not accompanied by any marked change in the composition of the sap; (5) the sugar content of the apples from ordinary storage is consistently higher, in spite of their more rapid respiration, than that of the apples from cold storage.

The work in progress consists of (a) a more complete analysis of the carbohydrates present; (b) the relation between the amounts of pectin present in the juice and the cell wall; (c) the relation of free and combined organic acid. In connection with this work, Dr. S. B. Schryver has investigated a method for the determination of small quantities of methyl alcohol with a view to the estimation of the pectin.

Dr. W. Brown has been engaged at the Imperial College of Science and Technology upon a determination of the minimum temperatures for the growth of the fungi commonly occurring in fruit storage, where also an examination of the effect of the amount of available nutrient on the position of the minimal temperature has been carried out.

The effect of various concentrations of carbon dioxide on the germination and the growth-rate of fungi on different culture media at various temperatures has also been studied.

At Long Ashton, Professor B. T. P. Barker and Mr. C. P. Dutt have concentrated their attention upon the chemistry of the process of ripening in fruit. It is believed that the keeping qualities of fruits are largely affected by the changes undergone by their pectin contents. Since Fremy's original investigations on this subject little work has been done in this direction, and the present investigation has been undertaken with the object of obtaining further information on the nature of these substances and their significance in ripening.

The work done during the last fruit season may be grouped under the following heads:—

- (1) Chemistry of Pectins.
- (2) Enzyme action.
- (3) Histological and microchemical observations.

(1) It appears well established that the tissues of unripe fruit contain material insoluble in water which, as ripening proceeds, undergoes change and yields a compound or compounds soluble in cold water and precipitable from aqueous solution by alcohol in characteristic gelatinous form. Fremy and most of the earlier subsequent workers on the subject have referred to the initial insoluble material under the name of pectose, and have termed the soluble product pectin. The latter, according to Fremy, undergoes a series of further changes as ripening proceeds resulting in the presence in ripe fruit of a complex mixture of substances, which he claims to have isolated, and the characters of which he has described in some detail. Notwithstanding the work of numerous investigators, there is at present no general agreement as to the chemistry of the group, and there is still uncertainty as to which, if any, of Fremy's products are definite compounds, and which are mixtures of a more or less complex character. No other worker has followed in detail the series of changes in the pectinous contents of fruit

during ripening, and it seemed desirable therefore at the outset of the present investigation to confirm, if possible, Fremy's observations as to the general character of the changes before investigating the nature of the change at each step of the series more closely.

The following notes serve to indicate the results observed, which in general are as described by Fremy. For the sake of convenience of description his nomenclature has been largely followed, but it must be understood that this does not imply the acceptance of his views as to the existence of the substances referred to as definite chemical compounds.

In early stages of ripening an aqueous extract of fruit tissues gives little or no gelatinous precipitate with alcohol. This precipitate, indicating the presence of water-soluble pectin, begins to appear when the fruit softens and increases in amount as the fruit ripens. In later stages of over-ripeness the amount of pectin decreases, and it may disappear altogether.

The properties and reactions of the pectinous material have been studied at different stages during the above series of changes, and have been found to agree closely with the properties and reactions of the products obtained by the chemical hydrolysis of pectin.

In the water soluble stage, precipitable by alcohol, the amount that can be precipitated by neutral lead acetate solution (corresponding to Fremy's parapectin) was found to increase as ripening proceeds. In the over-ripe stages precipitation with barium chloride was possible in some cases (corresponding to Fremy's metapectin).

The formation of an insoluble product by the action of acid or alkali on pectin corresponds to the formation of an insoluble pectinous substance by the action of the enzyme pectase on pectin solutions. In typical cases the gel, when first found by the action of pectase, is soluble in hot dilute acid, and, after treatment with acid in the cold, is soluble in boiling water, the solution giving a jelly on cooling. This jelly corresponds in its properties with the pectic acid of Fremy. On standing the gel produced by pectase action usually contracts with extrusion of liquid and in this stage is insoluble in acid, or subsequently in water. The insoluble substance after treatment with acid corresponds in its properties with the pectic acid of Fremy.

This "pectic acid" dissolves readily in solutions of many neutral organic salts such as ammonium oxalate. The solution in ammonium oxalate yields a gelatinous precipitate with alcohol which has many points of resemblance to the "pectinogen" prepared by Dr. S. B. Schryver.

The disappearance of pectin from the fruit seems to be accompanied by an increase in the amount of an acid substance which is soluble in water but not precipitable by alcohol, and agrees in its properties with the product obtained by continued hydrolysis or pectin by acid, which was described by Fremy under the name metapectic acid.

(2) Evidence has been obtained of the activity of an enzyme concerned in the production of soluble pectin from the insoluble substance of the cell wall.

Experiments have been made on various fruits at different stages of ripeness, but it has not been

found possible up to the present to isolate the enzyme having this action. By using expressed juices, water extracts of fruit and tissue residues after the expression of the juice, water extracts of fruit and tissue residues after the expression of the juice, evidence has been obtained which indicates the presence of a pectose-dissolving enzyme. For the most part soft fruits and plums have given negative results, but successful experiments have been made with apples and pears. Further experiments with these fruits are in progress.

Some study has also been made of the conditions under which the enzyme pectase is able to act on pectin solutions yielding an insoluble pectinous substance. In some cases, a jelly-like clot of this material is produced, the formation of which is dependent on the concentrations of pectin and pectase and on the presence or absence of acids or other inhibiting substances.

The setting action of pectase is destroyed by heating to a sufficient temperature. For a comparison of the activity of the pectase in different fruits experiments were made to determine the upper temperature limit. The pectase power of different fruits varied considerably, the chief determining factors being probably:—

- (a) the amount of pectase;
- (b) the presence of inhibiting substances.

Usually the ripe fruit was most active.

On the whole, the action of the pectase of the unripe fruit is inhibited by heating to a lower temperature than required by the ripe fruit.

(3) Some observations with the microscope were made on sections of fresh material, particularly by means of a staining reaction with ferri ferricyanide, which depends on the reducing power of pectin compounds.

It has been found that observations could be made as exactly and more conveniently on material preserved in alcohol and sectioned in paraffin wax by the usual microtome method. For the various fruits studied, therefore, a progressive series at different stages of ripening has been preserved in alcohol so as to be ready for use when required.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 4, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE following papers were read:—

"Vibrations of an Elastic Plate in Contact with Water." By Prof. H. LAMB.

The chief problem considered is that of determining the gravest frequency of a thin elastic diaphragm filling an aperture in a plane rigid wall which is in contact on one side with an unlimited mass of water. This had an interest in connection with submarine signalling. An exact solution is not attempted, but a sufficient approximation for practical purposes is obtained by Rayleigh's method of an assumed type, which gives good results if the type be suitably chosen. The rate of damping owing to the loss of energy

by sound-waves generated in the water is also investigated. The gravest mode of vibration with a nodal diameter is also treated in a similar manner. The comparison with the previous case shows how the effect of the inertia of the water and the damping, are both diminished by the freedom of lateral motion near the surface between the two segments which are at each instant in opposite phases.

"The Transmission of Electric Waves around the Earth's Surface." By Prof. H. M. MACDONALD.

"A Re-examination of the Light Scattered by Gases in respect of Polarisation. II.—Experiments on Helium and Argon." By Lord RAYLEIGH, F.R.S.

The light scattered by helium and by argon is investigated. It is found in the case of helium that the total light scattered is in accordance with what would be expected from its refractivity. The polarisation in helium, contrary to what was found in 1918, is approximately complete. No intensity was detected in 24 hours of exposure in the component vibrating parallel to the exciting beam, and certainly this component was less than 0.5 per cent of the other.

Argon polarises much more completely than any other gas examined, with the possible exception of helium, the weak component being only 0.4 per cent of the other.

"Dilatation and Compressibility of Liquid Carbonic Acid." By Prof. C. F. JENKIN.

The paper describes the measurement of the dilatation and compressibility of carbonic acid between temperatures of -37° C. and $+30^{\circ}$ C. and up to pressures of 1400 lb. per square inch. The measurements were made to supply accurate data for determining the starting point for drawing the p and l diagrams and to replace the approximate results (known to be inaccurate) given in a former paper (*Phil. Trans.*, A, ccxiii, 76).

The apparatus consists of an inverted burette dipping into mercury, the whole enclosed in a steel cylinder. The volume occupied by the CO_2 in the burette was indicated by the resistance of a long loop of platinum wire, short circuited at the bottom by the mercury. The temperature was indicated by a second platinum wire, wound round the upper end of the burette, used as the "bulb" of a platinum thermometer. The pressure was shown by a large calibrated bourdon pressure gauge. The results are given in tables and curves showing (1) the specific volumes of CO_2 at varying pressures and temperatures; (2) the true coefficients of expansion $\frac{1}{v} \left\{ \frac{dv}{dt} \right\}_p$; and (3) the true coefficient of compressibility, $\frac{1}{v} \left\{ \frac{dv}{dp} \right\}_t$.

The investigation was undertaken for the Food Investigation Board (Board of Scientific and Industrial Research).

"Radiation in Explosions of Hydrogen and Air." By W. T. DAVID.

This paper contains a record of the results of experiments on the emission of radiation during the explosion and subsequent cooling of mixtures of hydrogen and air contained in a closed vessel. The results of experiments on the transparency of the exploded mixtures are also recorded. Some

of the main conclusions arrived at are as follows:

- (i) The rate of emission is approximately proportional to the fourth power of the absolute mean gas temperature.
- (ii) The maximum rate of emission occurs at the point of maximum temperature.
- (iii) The exploded mixtures are very transparent throughout cooling to radiation of the same kind as they emit.
- (iv) The intrinsic radiance increases both with the lateral dimensions and with the thickness of the radiating layer of gas.
- (v) The 2.8μ band of steam ceases to be emitted when the gas temperature has fallen to about 700° C.

The experiments indicate that radiation phenomena in the hydrogen mixtures are in general similar to those in coal-gas mixtures (*Phil. Trans.*, A, ccxi, 375-410). In one or two respects, however, there are important differences, the most noticeable of which perhaps is, that in the hydrogen mixtures the maximum rate of emission occurs at the moment of maximum temperature, whereas in the coal-gas mixtures it occurs during the explosion period (during which the bulk of combustion takes place). This is of interest in its bearing on the nature of combustion.

The ceasing of the emission of 2.8μ radiation after the gas temperature has fallen to about 700° C. indicates that the vibratory degrees of freedom of the steam molecules corresponding to radiation of this wave-length, share in the heat energy of the molecules only at temperatures above 700° C. This would appear to account for the rapid rate of increase of the specific heat of steam which begins to take place in the neighbourhood of this temperature.

"Photochemical Investigations of the Photographic Plate." By R. E. SLADE, D.Sc., and G. I. HIGSON.

"The Relationship between Pressure and Temperature at the same Level in the Free Atmosphere." By E. H. CHAPMAN, D.Sc.

The paper deals with the exceptionally high values contained in the table of coefficients of correlation between changes of pressure and changes of temperature at different levels in the atmosphere included in Geophysical Memoir 13 of the Meteorological Office, by W. H. Dines. The coefficients are computed for observations taken at random, and arranged in four groups for the year, of three months each.

For the layers between 4 kilometres and 8 kilometres these coefficients range from 0.75 to 0.92. It is assumed that if the observations were freed entirely from errors of measurement the coefficients would be still higher. A method is therefore worked out for correction of coefficients of correlation for probable errors of observation in measurement.

An estimate is formed of the extreme values of the errors and the probable errors in the measurement of temperature and pressure in the atmosphere by an examination of the results obtained by Dines in England and Blair in the United States, and from the values a table of ratios for the correction of the crude values of the several coefficients is obtained. The final table of coefficients for the range from 4 kilometres to 8 kilometres, as corrected for probable errors of observation, contains 20 values each referring to 3

months. All of the 20 trimestal values thus treated come out greater than 0.84, 18 of them exceed 0.9, and 3 of them reach the maximum value of 1.0.

"Note on Vacuum Grating Spectroscopy." By Prof. J. C. McLENNAN, F.R.S.

INSTITUTION OF MINING AND METALLURGY.

October 21, 1920.

Mr. FRANK MERRICKS, President, in the Chair.

"The Origin of Primary Ore Deposits." By J. MORROW CAMPBELL.

The author commences at the period when the outer silicate shell of the earth was molten. The primæval magma is regarded as having been practically homogeneous and containing about 60 per cent of combined silicates. All water was then in the atmosphere giving a pressure over 300 times as great as at present. As temperature fell water and oxygen were absorbed; crust-formation, foundering, and resorption went on for a long period producing a flat temperature gradient in the liquid. Viscosity eventually rendered further foundering impossible, the crust became permanent, granite developed and below it the segregated basaltic magma long remained liquid. At this stage the isostatic balance was adjusted. Ore minerals in large quantity were given off at the surface of the granite; these were denuded and dispersed in sediments and solution. This, with subsequent absorption by intruded basic magma is assumed to have been instrumental in causing the present erratic distribution of primary ores. All so-called water in magmas is held to exist in combination as hydroxyl with silica not in solution as a gas.

Magmatic differentiation is regarded as having been caused by the agency of silicic acid—silicon combined with hydroxyl—which extracts potash aluminosilicate producing a solution lighter than and immiscible with a melt of basic feldspars and ferro-magnesian minerals. It is believed that in this way the first great split of primary magma into the world-wide granitic and basaltic types was brought about.

Evidence regarding the existence of silicic acid in magmatic liquids and elsewhere in nature is recited.

The ultimate result of the action of water on rock magmas is that silicates are completely removed and a residue of ore minerals such as magnetite, ilmenite, and chromite left.

Vein fissuring was brought about in and above batholiths by the expansive force due to the increase in solid specific volume of various elements. This increase is very considerable, exceeding in amount the contraction on solidification of the granite, and continues throughout the whole of the crystallisation period. The effect of this force appears in waves as fissures in successive series. These developed very rapidly, were instantly filled with magmatic mother-liquor and quickly sealed by the deposit of solids therefrom.

Quartz is almost always present in veins along with ore minerals, and silica often occurs in solution in thermal springs, especially such as carry gold, arsenic, antimony, and mercury. For these and other reasons it is regarded as probable that primary ore minerals passing up from magmas to veins do so in silicic acid solution and possibly in combination. The deposition of these ores is usually caused by loss of heat and reduction of pressure. It is believed that there are definite but narrow limits of temperature between which each ore mineral develops. These correspond to the temperatures in the strata at the bottom and the top of the ore at the time of deposition. Ore persisting for a vertical depth of 2000 feet would therefore indicate normally a temperature range of 20° C.

The pneumatolytic theory of the origin of the high temperature ores is rejected because the phenomena of their occurrence is quite inconsistent with what would result if these metals had been given off as gases by magmas. The boiling point of tungsten fluoride (19° C.) and tin fluoride (705° C.) are so far apart that it would be impossible for wolfram and cassiterite to have developed in contact with one another as they frequently do. Accessory minerals such as fluorite and tourmaline lose the genetic significance usually attached to them owing to the fact that they are not invariably present with tin and tungsten ores and are frequently associated with a variety of other ores which are admittedly of hydrothermal origin.

In introducing the paper the author called attention to the probable importance of variations of pressure in ore solution and deposition. Separation from simple solution would involve deposition of ore along the whole upward course of the solvent. This does not take place, the end being usually abrupt in an upward direction. The phenomena in nature seem to indicate that reduced pressure causes dissociation and, at some point, the total removal of ore from solution. High temperatures and pressures are not entirely correlative, and, since they usually accompany one another in nature, it is possible that as regards ore deposition we may in the past have been confusing the two.

CORRESPONDENCE.

VICTOR MEYER'S APPARATUS.

To the Editor of the Chemical News.

SIR,—The outer tube of this apparatus seems to be always of glass, for those which I have seen have been of that material, and text-books and apparatus makers' catalogues show glass. No doubt others have been troubled with students breaking the bottom of the outer tube, which is necessarily thin. I suggest to them that they should adopt a tube made of sheet copper, with a dished bottom, which can be used with water or any liquid which does not attack copper. A copper tube costs more than does a glass tube, but my experience has been that it soon proves itself more economical. Perhaps makers of apparatus may take the hint.—I am, &c.,

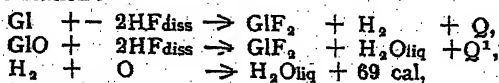
A. PRICE.

Technical School, Barnsley.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. No. 14 (October 4, 1920).

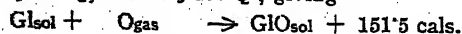
HEAT OF OXIDATION OF GLUCINUM.—MM. H. Copaux and C. Philips.—The glucinum for the above research was prepared according to the method laid down by Lebeau (*Compt. Rendus*, 1898, cxxvi., 744). Many methods were tried by the authors before a satisfactory one was obtained. They first tried to determine the heat of oxidation of glucinum by direct combustion, but no satisfactory results were obtained, because there always remained behind some unconverted metal. They tried the addition of a small quantity of vaseline, also using a known weight of cotton, but without any result. The addition of oxide of lead was also tried; this was found to be useless, for it left after combustion, small particles of reduced lead which had not reoxidised. The method they finally adopted was to measure the heat of solution of both the metal and oxide in the same acid. Hydrofluoric acid, being the only acid capable of dissolving both glucinum and anhydrous glucina quickly, was adopted. The following thermochemical equations will give the required heat of formation:—



from which



After a series of experiments the authors adopted 100 for Q, and 26.5 for Q¹, giving



Thus, glucinum becomes classified immediately after calcium (160), and before lanthanum (148.2), magnesium (144), aluminium (128.6), cerium (112), &c.

Bulletin de la Société Industrielle de Rouen.
Vol. 48, No. 2.

ALSATIAN POTASH SALTS.—In Alsace, potash deposits exist around Mulhausen, also around Wittelsheim. They extend from the north-east of Mulhausen to the foot of the Vosges Mountains, the best potash being found at a depth varying from 400 to 600 metres. The deposits have been estimated to contain 300 million tons of potash. The potash veins exist in alternate layers of red and grey colour. They are composed of a mixture of sylvine or potassium chloride and rock salt or sodium chloride, the mixture being known as sylvinit. The colour of the red layers is caused by oxide of iron; these veins are richer in potash than the grey veins, which contain a larger amount of rock salt. The content of KCl varies from 20 per cent to 60 per cent. The Alsatian salts are very pure, containing little magnesium salts which are injurious in agricultural work, consequently they need only a simple grinding, differing from the Stassfurt carnallites which must necessarily be purified. Two specimens of sylvinit gave 14 per cent K₂O (22 per cent KCl) and 20 per cent K₂O (32 per cent KCl). (A very complete account of the potash mines of Alsace is published in the *Bulletin de la Société Industrielle de Mulhouse*, No. 4, April, 1912).

NOTICES OF BOOKS.

Margarine. By WILLIAM CLAYTON, M.Sc. (Liverpool). Pp. xi.+187. 1920. London: Longmans, Green, & Co., 39, Paternoster Row. Price 14/- net.

THIS volume adds one more to the "Monographs on Industrial Chemistry," edited by Sir Edward Thorpe, C.B., LL.D., F.R.S. The author, in this exceedingly interesting monograph, deals with a subject which has hitherto only been dealt with by other authors as a subsidiary subject, that is to say, only a few pages have been reserved to describe this important industry.

In an introduction is given a brief history of the industry, followed by a chapter on the "Oils and Fats used in Margarine Manufacture." The manufacture of margarine is next discussed, where is given the different processes adopted, illustrated by diagrams. The chemistry of its constituents is next discussed, and the methods of their analysis, as well as of the finished product. A chapter on "Nutritional Chemistry" deals with the recent investigations on the Vitamines.

A bibliography and an index complete a book which should prove useful to all who are interested in this industry.

NOTES.

CROP YIELDS OF THE NORTHERN HEMISPHERE IN 1920.—The October Statistical Bulletin of the International Institute of Agriculture announces the aggregate results of cereal crops in most of the countries of the northern hemisphere. Data are now to hand from almost every quarter, with the exception of Russia, but as regards Europe comparisons with previous seasons cannot be made complete, owing to the numerous territorial alterations. The totals resulting from available and comparable data for the northern hemisphere sum up to 56.8 million metric tons of wheat, and 5.6 million tons of rye, in the aggregate 62.4 million tons. This quantity is slightly larger than the yield in 1919 (61.7 million) and identical with the average of the preceding five years. The comparable data for barley dealing with a number of countries producing just under one-half of the world's yield, make a total of 12.7 million tons, 8 per cent larger than the production of 1919, and 5 per cent below the five years' average. The yield of oats in countries furnishing all the required data (affording about 60 per cent of the world's yield) is estimated at 38.3 million tons, showing an increase of 21 per cent over last year, and 9 per cent over the average. The maize crops of South-Eastern Europe are reported as good, that of Italy as fair, while the United States' yield amounts to 81.7 million metric tons, 10 per cent over last year's, and 16 per cent above the average. Reports on the probable yield of beet sugar are favourable from Austria, Belgium, France, Germany, Italy, Netherlands, Sweden, and Canada, also for both cane and beet sugar from the United States. The export from British India of 400,000 tons of wheat has been sanctioned and will take place unless internal prices advance beyond the purchase limit officially fixed. The weather in October has not been favourable for crop developments.

Blackie's New Books in Science & Philosophy

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TIDAL LANDS A STUDY OF SHORE PROBLEMS

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The contributors include: W. M. Bayliss, F. G. Hopkins, E. Margaret Hume, A. R. Cushny, K. J. J. Mackenzie, E. J. Russell, R. G. Stapledon, A. S. Horne, Sydney J. Hickson, A. G. Tansley, Lt.-Col. Martin Flack, R. C. M'Lean, F. W. Oliver, H. M. Vernon, Henry Kenwood. Price 5s. net.

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—*Spectator*.

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MEETINGS FOR THE WEEK.

- Monday, November 22.*
Institution of Electrical Engineers, 7.30. (At Sheffield).
- Tuesday November 23.*
Institution of Petroleum Technologists, 5.30.
Institution of Electrical Engineers, 7. (At Manchester).
- Wednesday, November 24.*
Institution of Electrical Engineers, 6. (Wireless Section).
Society of Chemical Industry, 7. (At Nottingham).
Royal Society of Arts, 8. "Colour Vision and Colour Blindness"
by Dr. F. W. Edridge-Green.
Institute of Chemistry, 8. "Some Scientific Aspects of Tanning,"
by J. Turney Wood.
- Thursday, November 25.*
Royal Society, 4. "The Growth of Seedlings in Wind" by Prof. L. Hill.
"The Effect of Thyroid-feeding and Thyro-parathyroidectomy upon the Pituitrin Content of the posterior Lobe of the Pituitary, the Cerebro-spinal Fluid, and Blood" by Prof. P. T. Herring.
"Reflex Times in the South African Clawed Frog" by W. A. Jolly.
"Cellular Immunity. Observations on natural and acquired Immunity to Cobra Venom" by Prof. J. A. Gunn and R. St. A. Heathcote.
"Studies on Synapsis" by L. T. Hogebein
Society of Chemical Industry. (At Birmingham).
Institution of Electrical Engineers, 6.
- Friday, November 26.*
Optical Society and Physical Society, 7.30.

NOTICES.

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8th November, 1920.

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3163.

EDITORIAL.

WE have received the following important letter for publication:—

BRITISH CHEMICAL GLASSWARE.

SIR,—I feel that a brief history of the Chemical and Scientific Glassware Industry may be of some interest to your readers and show them very good reasons why they should insist, at all times, upon using British-made glass and apparatus.

The manufacture of chemical glassware was unknown in this country prior to the war, but was undertaken by several glass makers at the express desire of the Government. I doubt very much if at that time they quite realised the immense task they had undertaken, or the difficulties they would have to overcome. It must be remembered that there were very few manufacturers in this country with any knowledge of this particular branch of the glass industry, and little or no skilled labour was available. It was an extremely difficult task to attempt. However, after nearly six years of experimental and research work, involving a large expenditure of capital, the British manufacturers have succeeded in producing laboratory ware equal, and in some cases, superior in quality to the best known German makes.

In the early days of the war promises were very freely made that some assistance would be given to manufacturers in order that the industry would be kept in Great Britain, and that the country should not again be dependent upon foreign countries for supplies of glass so vital to the progress of industries and to the defence of the nation. This is very briefly the history of the industry up to the end of the war. We have succeeded in our task and have proved in yet another instance that to chemical glassware the label "it can only be well done in Germany" has been falsely applied.

In spite of all the work done to keep this industry in the country, manufacturers are viewing the future with great consternation. Germany is making a very desperate endeavour to regain her control of this important market, and helped as she is by the existing rate of exchange and other causes, hopes very shortly to encompass the death of the industry in this country. The position is a very serious one, not only from the point of view of the manufacturers, but also of the nation at large. I do not know of a single industry which can successfully continue without laboratory ware. This manufacture is essentially a "key" industry, and as such should be kept in the country.

Early in the war the country was in a very dangerous position owing to the lack of supplies of glass, and steel manufacturers stated that they could no longer continue the production of steel for guns unless they were given immediate supplies of glass. Whether it was by mere accident or the deliberate design of Germany, we perhaps shall never know, but very shortly after the outbreak of hostilities, it was discovered that stocks

of chemical glassware in this country, usually very considerable, were extremely low. It is obvious that this condition of affairs should never be allowed to re-occur; yet what is happening at present? Germany is flooding the country with the glass apparatus, in many cases at less than the cost of manufacture of the actual glass from which the apparatus is made here. An example of this came to my notice a few days ago, the articles in question were German test tubes which were offered at 2s. 7d. per gross. The cost of the glass tubing alone from which these test tubes are made in this country, is, in this country, 6s. 8d. per gross. So long as the rate of exchange stands as it is at present, Germany will be able to continue competition under these unfair conditions against British manufacturers. The price is cheaper, and many consumers in this country continue to buy foreign-made glass simply because it is less costly. Were the German exchange to-day normal, the price of their glass would be extremely high. This is a very important point; sooner or later the mark will again become more or less normal, and there will be no limit to the prices which they will be able to charge for their glass, because unless some assistance is given to prevent the manufacture of these goods being forced out of the country there will be absolutely no competition against Germany, therefore, no limit to the prices she may extort.

I do not deny for one moment that in the earlier days of the industry much inferior glass was produced. This was only to be expected, and does not surprise those who were connected with the industry, but that period is now passed for ever.

I earnestly appeal to your readers, the majority of whom are interested in chemical glassware, to insist on being supplied with British-made glass, *but it must be branded with the mark or name of the maker.* There is a quantity of unmarked glass still being offered, the origin and quality of which is doubtful.

The Government is being strongly urged to provide protection for this industry for a period of years to enable it to be placed on a satisfactory basis, when it will be in a position to meet any competition that may come from the Continent. In the meantime it is essential that users give their support to this important home industry.—I am, &c.,

T. LESTER SWAIN.

THE PHYSICS AND CHEMISTRY OF COLLOIDS AND THEIR BEARING ON INDUSTRIAL QUESTIONS.*

SOME OBSERVATIONS ON PEPTISATION AND PRECIPITATION,

By N. G. CHATTERJI and N. R. DHAR.

IN his article on peptisation and precipitation, Bancroft (second B.A. Report on Colloid Chemistry, 1918, p. 2) enumerates a large number of cases of peptisation. We have reinvestigated some of these reactions and come to the conclusion that in several cases the observations are not accurate. Thus we have found that silver chloride, silver chromate, and calcium silicate are not peptised in presence of a concentrated solution of cane sugar.

*A General Discussion before the Faraday Society and the Physical Society of London, October 25, 1920.

What actually takes place is that, in presence of a concentrated solution of cane sugar or glycerin, the precipitate does not come down immediately. It only does so on keeping for some time. But if it is centrifuged and specially a little diluted, the precipitate settles down at once. It therefore appears doubtful that peptisation at all takes place in these cases. True peptisation cannot give any precipitate when centrifuged in this way.

We have been successful in bringing about peptisation of a large number of hydroxides by means of glycerin, concentrated solutions of cane sugar or grape sugar. Thus the hydroxides of iron, nickel, thorium, mercury, cobalt, &c., have all been peptised by adding a caustic alkali to the solutions of salts of these metals in presence of glycerin or sugar. In the case of uranium and gold, ammonium hydroxide should be used instead of caustic soda. In none of these cases any trace of sedimentation could be observed even after vigorous centrifuging. One curious fact in this connection seems to have remained unnoticed. It is generally recognised that a substance which can peptise another during the formation of the latter may not be able to do so when once the substance has been formed. We have now observed that not only is the above true, but that peptisation can only be brought about if the alkali hydroxide is added to the mixture of the salt solution and glycerin. On the other hand, precipitation at once takes place if the solution of the salt is added to the mixture of glycerin and alkali hydroxide. Peptisation does not seem to take place in the case antimony hydroxide, copper fluoride, or barium sulphate.

A reference to the literature on the subject of peptisation shows the confusion that exists in this branch of chemistry. The nature of the solutions obtained by dissolving aluminium hydroxide, for example, in alkali hydroxides has been the subject of much discussion. The literature on the subject puts forth evidence in support of both the peptisation and chemical combination views. We have tried to solve the problem systematically by finding out whether any change in electrical conductivity of a solution of caustic alkali takes place when any of the hydroxides is dissolved in it. Incidentally, we have investigated the solubility of the hydroxides of copper, zinc, and cadmium in ammonia. We have found that a great increase in the conductivity of the ammonia solution takes place on dissolving these hydroxides. In this connection, it is interesting to observe that the cobalt-ammonium bases and the chromium-ammonium bases obtained by the double decomposition of a chloride of cobaltamine or chromiumamine by silver hydroxide are fairly strong bases (Cf. *Dhar Proc. Akad. Vetensk. Amsterdam*, 1920).

In the case of the action between sodium hydroxide and the hydroxide of copper, chromium, lead, zinc, aluminium, mercury, the following results are obtained. The conductivity of a solution of caustic soda did not appreciably change on the addition of hydroxides of chromium, aluminium, lead, mercury, whilst in the case of zinc the resistance of the caustic alkali solution appreciably increased when zinc hydroxide was dissolved in it. Hence we can conclude that the solutions of aluminium hydroxide, chromium hydroxide, lead hydroxide, mercury hydroxide, and copper hydroxide are cases of true peptisation

and not of chemical combination. On the other hand, in the case of zinc hydroxide, we get more of chemical combination than of peptisation. Or, in other words, the major part of the hydroxides of aluminium, chromium, copper, lead, and mercury exists in sodium hydroxide solution as a colloid, whilst the major part of zinc hydroxide remains as a zincate.

Bentley and Rose (*Jour. Amer. Chem. Soc.*, 1913, xxxv., 1490), from their experiments, were led to the conclusion that freshly prepared aluminium hydroxide dissolves in dilute acetic acid to form a colloidal solution. If this be true, our conductivity experiments ought to show no change in the conductivity if the acetic acid solution when aluminium hydroxide is added to it. But if an acetate is formed, the conductivity ought to increase considerably, for acetic acid, being a weak acid, has small conductivity, but its salts are good conductors. As a matter of fact, we have found that the conductivity of an acetic acid solution does not change appreciably when freshly precipitated aluminium hydroxide or ferric hydroxide or chromium hydroxide is dissolved in it, whilst the solution of zinc hydroxide in acetic acid causes a great increase in conductivity. Hence we can infer that the hydroxides of aluminium, chromium, and iron become peptised in acetic acid, whilst zinc hydroxide mainly forms zinc acetate with acetic acid. These results are corroborated by the fact that zinc hydroxide is a much stronger base than ferric, aluminium or chromium hydroxide.

We have already mentioned the peculiar behaviour of the products obtained by mixing together a metallic salt (capable of forming an insoluble hydroxide), ammonium or alkali hydroxide, and glycerin or a concentrated solution of sugar. We get or do not get a precipitate of the hydroxide according as we add the salt solution to a mixture of glycerin and hydroxide or the hydroxide to the mixture of the salt and glycerin. The clear solutions obtained in the latter case may be either due to the formation of a soluble compound of the hydroxide with glycerin or a colloidal solution of the metallic hydroxide. If a chemical compound is formed, new ions must appear, and the conductivity of the solution must differ from that of the one in which the metal gets precipitated as hydroxide, even though equal quantities of the reagents are taken in both the cases. But if the clear solutions are formed on account of the peptisation of the hydroxide in glycerin, there is, from the ionic point of view, no difference in the nature of the two solutions, and hence there should be no difference in conductivity of the two solutions.

Here are some experimental results:—

(1) *Cobalt nitrate, glycerin, and caustic soda.*

Solution in the Cell.	Specific Conductance
(a) Cobalt, nitrate glycerin and caustic soda—no precipitate	0.107
(b) The same precipitated	0.107

(2) *Nickel chloride, glycerin, and caustic soda.*

(a) Clear solution	0.094
(b) Precipitated solution	0.094

(3) *Mercuric chloride, glycerin, and caustic soda.*

(a) Clear solution	0.054
(b) Precipitated solution	0.053

Solution in the Cell.	Specific Conductance.
(4) <i>Ferric chloride, glycerin, and ammonia.</i>	
(a) Clear solution	0.0053
(b) Precipitated solution	0.0053
(5) <i>Uranium nitrate, glycerin, and ammonia.</i>	
(a) Clear solution	0.0021
(b) Precipitated solution	0.0021
(6) <i>Gold chloride, glycerin, and ammonia.</i>	
(a) Clear solution	0.0014
(b) Precipitated solution	0.0014

We find from the above that the conductivities of the two solutions are the same, and hence the ionic conditions of the two liquids are identical. We can, therefore, say with confidence that the clear solution is *not* due to the formation of any soluble complex, but only a peptised solution of the hydroxide. That they are really peptised solutions is further shown by the fact that a slight rise in temperature brings about a precipitation of the hydroxide, the same change also taking place if the solutions are kept for some hours.

When an alkali hydroxide is added to a solution of a copper salt, a blue hydroxide of copper is precipitated, which on warming becomes black, due, probably, to the formation of a compound less hydrated. But if during precipitation a trace of the copper salt remains undecomposed, the blue hydrate cannot be changed into the black one by any amount of boiling. The undecomposed salt cannot be completely removed by washing with cold water, and it seems probable that the undecomposed salt becomes absorbed by the blue hydroxide and stabilises it. Washing with hot water removes the undecomposed salt, and then the precipitate becomes black. We have observed that if to this black hydroxide a little of the copper salt be added and the whole boiled, a reversible change takes place and the blue precipitate reappears.

The next point for investigation was whether different alkali hydroxides have different actions on the stabilisation of the blue hydrate or not. In this connection certain striking observations were made. In order to make a rough quantitative idea, 1 cc. of $\frac{N}{20}$ copper sulphate or copper chloride solution was taken in every case, a measured amount of the alkali of known strength was run in from a burette, and the total volume was made up to 40 cc. in a boiling tube. The boiling tube was next put in a large beaker containing boiling water, and the time taken by each to turn black was noted. It must be emphasised that this being a case of reaction in heterogeneous medium, the results in some cases could not be exactly reproduced, but on the whole the following conclusions have been drawn from a large number of experiments:—

- (1) The stronger the alkali, the quicker is the transformation from the blue to the black modification; thus taking equal concentrations of KOH, NaOH, Ba(OH)₂, Sr(OH)₂, Ca(OH)₂, and aniline, it was observed that KOH blackened first. It was also observed that KOH transformed much more quickly than NaOH.
- (2) The behaviour of calcium and strontium hydroxides is very peculiar. Here with an excess of alkali there are more than one stage at which a complete retardation of the change

from the blue to the black form takes place. Thus, starting with a slight excess of the alkali, if we gradually increase the quantity, we find that the time taken to turn black gradually increases, reaches a maximum, and then decreases. With very large excess there appears to be a good deal of retardation.

Ammonium chloride and ammonium sulphate seem to retard this change, whilst ammonium nitrate and potassium chlorate are without any influence.

It is well known that in presence of an alkali, the blue freshly precipitated hydroxide of cobalt becomes pink. Now this change is exactly of the same type as the conversion of the blue copper hydroxide to the black variety. In this case also a trace of the undecomposed cobalt salt, nitrate, for example, gets absorbed by the blue hydroxide and stabilises it, and we cannot get the pink variety of cobalt hydroxide if there is a little undecomposed cobalt salt left. Just as in the case of copper, warming of the black variety with a little copper salt regenerates the blue variety, in the case of cobalt warming of the pink form with a little cobalt salt also regenerates the blue variety, but in the latter case the cobalt hydroxide begins to be oxidised in presence of air.

All those salts which produce a hydroxide soluble in excess of caustic alkali, namely, salts of zinc, aluminium, tin, lead, &c., markedly retard the transformation of both the blue copper hydroxide to the black form as well as that of the blue variety of the cobalt hydroxide to the pink form. It seems probable that the presence of aluminium hydroxide, lead hydroxide, tin hydroxide, &c., in the colloidal state tends to peptise the cobalt hydroxide or the copper hydroxide.

Benedict (*Jour. Amer. Chem. Soc.*, 1904, xxvi., 695) casually observed that if an excess of a caustic alkali be added to the solution of a cobalt salt, the blue hydroxide which is at first formed does not change into the pink variety if a nickel salt be present. The greater is the retardation, the greater is the amount of the nickel salt originally present in the solution. Benedict did not give any explanation of this peculiarity, neither did he mention the action of other salts on the rate of transformation of the blue to the pink modification. The effect of the presence of salts like ferrous ammonium sulphate, zinc sulphate, manganese sulphate, ferric chloride, chromium sulphate, potash alum, nickel chloride, tin chloride, lead nitrate, cadmium chloride, copper sulphate, magnesium sulphate, calcium chloride, thorium nitrate, strontium nitrate, and uranium acetate has been investigated, and it has been observed that only the nickel salt produces a remarkable retardation. The next to produce the greatest retardation seems to be a calcium salt, but there is a great fall in retardation from nickel to calcium. The transformation of blue copper hydroxide to the black variety is also retarded by nickel salts. It is interesting to note that though a soluble nickel salt added to a cobalt salt before the addition of the alkali retards the change of the blue to the pink form, the reaction is not reversed upon the subsequent addition of the nickel salt to cobalt hydroxide. Neither is there any effect when nickel hydroxide is added instead of a soluble nickel salt, though undoubtedly the hydroxide of nickel is formed when excess of

alkali is added to a mixture of the salts of cobalt and nickel.

Many interesting cases of adsorption have been observed, we believe, for the first time. Thus, if to the solution of an aluminium salt excess of concentrated alkali is added, the hydroxide at first precipitated redissolves. Now if a few drops of ferric chloride are added, the precipitated ferric hydroxide collected and washed thoroughly with hot water. This ferric hydroxide is now treated with caustic soda and filtered. The filtrate is boiled with ammonium chloride, and a precipitate of aluminium hydroxide is obtained. This is explained by the fact that ferric hydroxide during its precipitation adsorbs some of the colloidal aluminium hydroxide which is not removed by washing with hot water. Similar results have been obtained with a zincate and ferric chloride, and chromium hydroxide in solution and ferric chloride. Again, if to a solution of chromium hydroxide containing an excess of alkali a few drops of magnesium sulphate be added, the precipitate of magnesium hydroxide is found to contain a good deal of chromium hydroxide which cannot be dissolved by sodium hydroxide.

Summary.

1. Silver chloride, silver chromate, calcium silicate, cupric fluoride, and barium sulphate when precipitated in presence of glycerin or concentrated sugar solutions are not peptised.

2. The hydroxides of iron, nickel, cobalt, thorium, and mercury can be peptised by adding a caustic alkali to the solutions of salts of these metals in presence of glycerin or concentrated sugar solution. In the case of gold and uranium salts, ammonium hydroxide should be used instead of caustic soda. In these cases peptisation can only be brought about if the alkali is added to the mixture of the salt and glycerin, but precipitation takes place if the solution of the salt is added to the mixture of glycerin and alkali. Conductivity experiments support these results.

3. The major parts of the hydroxides of Al, Cr, Pb, Hg, and Cu when dissolved in sodium or potassium hydroxide exists as a colloid, whilst zinc hydroxide mainly forms a zincate, shown from conductivity experiments. Similarly, the hydroxides of Al, Fe, and Cr form colloidal solutions in acetic acid, whilst zinc hydroxide forms zinc acetate.

4. The transformation of blue hydroxide of copper to the black variety and that of the blue hydroxide of cobalt to the pink form are changes of the same type, and are almost equally affected by different catalysts.

5. The hydroxides of Al, Cr, and Zn respectively are adsorbed by ferric hydroxide when the later is precipitated in presence of solutions of the hydroxides of Al, Cr, and Zn in caustic soda.

DISCOVERY OF CINNABAR.—The Department of Overseas Trade is advised by His Majesty's Consul at Antofagasta that a deposit of cinnabar has been discovered in the Aguas Blancas district at Chile, which is situated about 90 kilometres from Antofagasta. Claims have already been taken out to the extent of a square mile and examinations are being carried out by mining experts. The properties are conveniently situated close to the railway. The lay of the deposit is said to vary considerably and great secrecy is being maintained as to results shown up to date.

DETERMINATION OF MOLYBDENUM.

By J. P. BONARDI and EDWARD P. BARRETT.

(Concluded from p. 246.)

Comparison of Results by Volumetric (Potassium Permanganate) and Gravimetric (Lead Molybdate) Methods.

Acid Decomposition.—A series of determinations were made with duplicate samples of a molybdenum solution in order to compare the results of the volumetric and gravimetric methods.

The volumetric method was used for solutions obtained by decomposition of molybdenite ores and flotation products with aqua regia, followed by the addition of sulphuric acid and boiling to fumes. The solutions were cooled, diluted, made ammoniacal, and filtered to remove silica, iron, and alumina. The filtered solutions were acidified with sulphuric acid and passed through a Jones reductor, then titrated with potassium permanganate solution.

The gravimetric (PbMoO_4) method was used for solutions obtained by the decomposition with aqua regia of duplicate samples, as for the volumetric method. The solutions were cooled, made ammoniacal, and filtered to remove silica, iron and alumina, then acidified, and the molybdenum precipitated as PbMoO_4 .

Table V. shows the results obtained.

TABLE V.—Comparison of Gravimetric (PbMoO_4) and Volumetric (KMnO_4) Results, using acid decomposition for both methods.

Sample No.	Mo content by—		Sample No.	Mo content by—	
	Gravimetric method. Per cent.	Volumetric method. Per cent.		Gravimetric method. Per cent.	Volumetric method. Per cent.
1	0.060	0.063	9	0.439	0.425
2	0.080	0.077	10	5.700	5.780
3	0.069	0.074	11	5.550	5.580
4	0.071	0.068	12	8.390	8.530
5	0.086	0.095	13	2.000	1.900
6	0.092	0.102	14	6.560	6.480
7	0.112	0.139	15	0.203	0.208
8	0.100	0.114			

On low-grade material, such as the first eight samples given in Table V., the addition of lead acetate does not produce any perceptible precipitate, though a faint cloudiness may frequently occur. Neither does the tannic acid, outside indicator, show any change in colour. After boiling the solution, however, for at least 15 minutes, a precipitate is formed which on swirling the solution with a glass rod will collect on the bottom at the centre of the beaker. If, after the solution has been boiled for an hour and then permitted to stand over night, no precipitate is formed, it can be assumed that no molybdenum is present, otherwise, erroneous conclusions are made that none is present or a "trace."

One of the best ways for testing the accuracy of chemical analyses of products obtained in a concentrating mill treating molybdenum ores, is to total the molybdenum content of all the products made in any ore experiment, then calculate whether this footing corresponds with the content in the feed sample. In several series of analyses of flotation products obtained from molybdenite ores, the average deviation for footing the molybdenum content was less than 2 per cent, which vindicates the accuracy of the methods defined in this paper.

Acid Decomposition and Fusion with Sodium Peroxide.

In order to obtain a comparison of the methods of decomposition a series of tests was made of duplicate samples of molybdenite ores and flotation products. One set was decomposed by aqua regia and the molybdenum then determined by the gravimetric (PbMoO_4) method. The other set was decomposed by fusion with sodium peroxide and the molybdenum determined by the volumetric (KMnO_4) method. The results are given in Table VI.

TABLE VI.—Comparison of Gravimetric (PbMoO_4) with Volumetric (KMnO_4) results, using Different Methods of Decomposition.

Sample No.	Mo content from decomposition by	
	Aqua regia and determination of Mo by gravimetric (PbMoO_4) method. Per cent.	Na_2O_2 fusion and determination of Mo by volumetric (KMnO_4) method. Per cent.
1	9.25	9.32
2	1.74	1.79
3	0.88	0.80
4	0.32	0.45
5	0.10	0.14
6	0.07	0.09
7	0.06	0.08

Comparison of Volumetric (Lead Acetate) and Gravimetric (Lead Molybdate) Methods, using Fusion Methods of Decomposition.

As the titration of a dissolved molybdenum salt with lead acetate agreed closely with the gravimetric determination as lead molybdate for pure chemical solutions, these two methods were tried on low-grade ores that had been fused with sodium peroxide. When such a fusion is leached, practically all the silica and alumina will be found in the filtered liquid, besides other bases soluble in excess alkali. Several ores containing less than 1 per cent molybdenum sulphide were tested by titrating with a standard lead acetate solution, 1 cc. of which was equivalent to 0.00072 grm., or 0.072 per cent Mo on the basis of a 1-grm. sample taken for an analysis. The results were erratic and uncertain. Precipitating the molybdenum from the titrated solution and weighing as lead molybdate also gave variable results because, with lead acetate present in the ammonium acetate and acetic acid solution, much aluminium and silica is carried down with the lead molybdate. However, the gravimetric method described in this paper works well for molybdenum solutions that are free from these elements, as when ore is decomposed by acid.

Some of the difficulties given in standard textbooks regarding the titration of a low-grade lead ore with standard ammonium molybdate solution, which is the reverse of the procedure for titrating a low-grade molybdenum ore with a standard lead acetate solution, using an outside indicator of tannic acid, are as follows:—

1. The very low percentage of lead (or molybdenum) is difficult to determine on account of the slowness of the reaction.
2. The large amount of dissolved salts that is necessary in the analysis hinders the separation of lead as molybdate and obscures the end point obtained with tannic acid.

An excess of ammonium salts and ammonium acetate must be avoided, because if such excess is present the results obtained will be too high.

4. Iron, if present, gives a colour with tannic acid.

5. Calcium, barium, and several other bases, form more or less insoluble molybdates that interfere with the results.

6. The method is not accurate.

Removal of Interfering Elements.

Separation of Tungsten Trioxide from Molybdenum Trioxide.

Tungsten if present interferes with the gravimetric determination of molybdenum, as the tungsten is also precipitated by the lead acetate, but it may be removed from the ignited, weighed lead molybdate by treating with hydrochloric acid as described by Crookes (William Crookes, "Select Methods in Chemical Analysis," 1905, 4th ed., p. 196). He says: "The HCl solution of the ignited lead salts, to which a few drops of HNO_3 have been added, is evaporated, preferably over the water-bath, until nearly pasty, when the WO_3 filtered off. The weak acid precipitates any WO_3 still unseparated by the evaporation, and is yet strong enough to hold the molybdenum in solution."

Sulphuric acid has also been used. Regarding this method, Crookes (William Crookes work cited, pp. 196-197) makes the following comment: "Max J. Ruegenberg and Edgar F. Smith (M. J. Ruegenberg, and E. F. Smith, "The Separation of Tungsten Trioxide from Molybdenum Trioxide," *CHEMICAL NEWS*, 1901, lxxxi, 5; *Jour. Am. Chem. Soc.*, xxii, 772) effect the separation of tungsten from molybdenum as follows: Their process is based on a statement that tungstic acid is insoluble in concentrated or dilute sulphuric acid, hot or cold, whereas molybdenum trioxide is very easily and rapidly dissolved. Upon trial, it was found that sulphuric acid of specific gravity 1.378 dissolved molybdenum trioxide very readily and apparently did not affect the tungsten trioxide. Acid of this concentration was therefore used with the following mixture of the two oxides: 0.7355 grm. of tungsten trioxide and 0.0185 grm. of molybdenum trioxide were digested for a few minutes with 25 cc. of warm sulphuric acid. The insoluble portion was filtered out, and washed with water containing sulphuric acid. After drying, it was ignited and weighed. It equalled 0.7350 grm."

The other trials, conducted in precisely the same manner, were as follows:—

	2 Grms.	3 Grms.	4 Grms.	5 Grms.	6 Grms.
oxide taken	1.0368	0.0871	0.3588	0.8868	0.5996
Molybdenum trioxide taken	...	2.2712	0.6871	1.1836	1.1986
Tungsten trioxide found	1.0630	0.0870	0.3587	0.8866	0.5996

The filtrate containing the dissolved molybdic acid showed no tungstic acid upon examination.

These results indicate that where the two oxides are present together this mode of separation is of value and merits consideration.

Separation of Molybdenum from Vanadium.

If vanadium is present in the ore it can be removed as given under "Interfering Elements," or

be precipitated by lead acetate along with the molybdenum as lead vanadate. The ignited and weighed precipitate of lead molybdate and lead vanadate should be dissolved in HNO_3 , taken to fumes with H_2SO_4 to remove lead, and the vanadium determined according to the method of Moore and Kithil (Richard B. Moore, and Karl L. Kithil, "A Preliminary Report on Uranium, Radium, and Vanadium, *Bull.* 70, Bureau of Mines, 1916, pp. 90-91. W. W. Scott, "Standard Methods of Chemical Analysis," 1917, 2nd. ed., p. 282).

Separation of Iron.

The following method for the determination of molybdenum in ferromolybdenum by precipitation as PbMoO_4 is an improvement on the original method described by Strebinger (Robert Strebinger, "Ein Beitrag zur quantitativen Bestimmung des Molybdäns, als Bleimolybdat," *Chem. Zentralb.*, 1918, lxxxix., 378).

In this process 0.5 to 1.0 grm. of finely pulverised ferromolybdenum is fused in an iron crucible with sodium peroxide. The fusion is leached with water and the solution made up to 500 cc. and filtered. A sample of 100 cc. is taken and any iron present is removed by adding nitric acid and ammonia. The clear solution is acidified with 5 cc. excess hydrochloric acid. About 7 grms. of sodium or ammonium acetate is added, the solution diluted to about 300 cc., heated on a hot plate to about 80°C ., and the molybdenum precipitated by titrating this hot solution with a solution of lead acetate (about 18 grms. per litre), tannic acid being used as an indicator. To this 2 to 3 cc. excess of lead acetate solution is added, and 2 or 3 cc. of acetic acid; then the beaker is replaced on the hot plate for 15 or 20 minutes to allow the lead molybdates to crystallise and settle. The solution is filtered hot and washed well, with the precautions as explained under "Precipitation." The filter is ignited at a dull red heat, then cooled. The ignited lead molybdate is brushed out of the annealing cup on to the balance pan and weighed. The weight of lead molybdate times 0.2615 gives the weight of the molybdenum.

This modification makes the method much shorter, because it eliminates two periods of 6 and 12 hours, respectively, that must otherwise be allowed for the settling of the precipitated lead molybdate.

Separation of Other Elements.

The separation of molybdenum from the alkalies, alkaline earths, metals of the ammonium sulphide group, metals of Group II., etc., is described in detail by Treadwell and Hall (F. P. Treadwell, and W. T. Hall, "Analytical Chemistry," 1912, 3rd ed., vol. ii., pp. 286-289).

Conclusions as to Gravimetric Method.

1. This method is applicable to high-grade as well as low-grade material.
2. The molybdenum is readily converted to ammonium molybdate and obtained in a solution practically free from silica, iron, and alumina, and also from lead, if the sample has been fumed with sulphuric acid.
3. Sulphates do not interfere with the determination.
4. A very short time is required for precipitation of the molybdenum as lead molybdate.
5. The precipitate is easily filtered and washed.

6. No special precaution is necessary.
7. No special manipulative skill is required.
8. No special equipment is necessary and no standard solutions are needed.
9. The method is not as rapid as titration with potassium permanganate, following fusion with sodium peroxide and reduction in a Jones reductor.
10. The method is not practicable when fusion is necessary to decompose the ore (F. W. Horton, "Molybdenum: Its Ores and their Concentration," *Bull.* 111, Bureau of Mine, 1916, p. 41).

REPORT FOR THE YEAR 1919 OF THE FOOD INVESTIGATION BOARD DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

(Concluded from p. 247.)

Oils and Fats Committee.

THE work of this Committee has been carried out at the University of Liverpool, under Dr. R. Robinson, F.R.S.; at the University of Manchester, under Professor A. Lapworth, F.R.S.; at the University of St. Andrews, under Professor J. C. Irvine, C.B.E., F.R.S.; and at the College of Technology, Manchester, under Dr. L. G. Radcliffe. At the Lister Institute, Dr. Ida Smedley MacLean has investigated the formation of fat by micro-organisms.

The work consists in part investigations begun during the war, at a time when there was the possibility of an acute conflict between the demands for oils and fats for human consumption on the one hand, and for the preparation of the glycerol needed for propellant explosives on the other. At and after the Armistice there was a change in the situation, but the investigations were continued from the point of view of an insurance for the future as well as on account of their intrinsic interest.

Dr. Robinson and Miss F. Pollecoff have investigated the classical glycerol synthesis *via* propylene which, from the point of view of yield, was found to be unsatisfactory at more than one stage. For instance, the bromination of propylene dibromide with formation of tribromopropane gave a poor yield, considerable amounts of isomerides of tribromhydrin being formed as bye-products. The results obtained up to the time when this particular research was abandoned indicated that a convenient and technically applicable synthesis of glycerol must be an entirely new one. Professor Lapworth and Miss E. Heyworth studied the influence of conditions on the mode of union of hypochlorous acid with unsaturated carbon compounds, as it seemed probable that the acid might assume great importance in connection with the chemistry of glycerol and fats. Numerous quantitative measurements, in particular of velocity of reaction, were carried out, and a number of data were obtained having a direct bearing on the question of the mechanism of the reactions. The enquiry is as yet only in its preliminary stage, but gives promise of interesting developments. Dr. Robinson made a series of experiments, in which the starting-point was an aqueous solution of

formaldehyde, with the object of arresting the condensation of formaldehyde at the stage of glycollaldehyde or glycerose, which may perhaps be regarded as the intermediates in the synthesis of hexoses. Reducing agents, such as sodium amalgam, were introduced into the alkaline condensation mixture, but in no case was the formation of glycol or glycerol observed. A possible explanation is that the intermediate stages condense further with far greater readiness than formaldehyde, and are perhaps also difficult to reduce. It was noticed that benzoylmandelonitrile yields benzoyl benzoin when it is treated with sodium ethylate in alcoholic solution, and the corresponding reaction with benzoylglycollonitrile (from benzoyl chloride, formaldehyde, and potassium cyanide) was attempted, especially since it would seem that the initial reaction in the synthesis of hexoses from formaldehyde must be of the benzoin type. The product of the reaction was isolated as an osazone and identified as an acrosazone, produced in notable amount and probably more smoothly than is possible in other methods starting with formaldehyde. Again it seemed that the glycollaldehyde possibly produced in the reaction was too sensitive to alkali and condensed to a hexose.

Attempts were then made to use a regulated Knoevenagel reaction in order to control formaldehyde synthesis, and although this has not yet resulted in the discovery of a route to glycerol, an observation of considerable general interest was made, and the matter was followed up on this account. It is possible that some of the substances made may be of interest in various directions, for example, as alternatives to hexamethylene tetramine as urinary antiseptics. The compounds all yield formaldehyde on hydrolysis, some slowly with water, others with acids. The action of formaldehyde on an equivalent of a secondary base is to produce a compound of the form R_2N-CH_2OH , which condenses with various substances, eliminating water and introducing the group R_2N-CH_2 . With alcohols and mercaptans now semiacetals and sulphides are formed of the general formulæ R_2N-CH_2-OR (SR). These substances are mobile liquids which boil without decomposition at the usual pressures, and undergo condensations with many other substances, an alcohol or a mercaptan being eliminated. A representative number of these compounds were prepared and analysed.

At about this stage Dr. L. G. Radcliffe made a discovery which pointed the way to a successful glycerol synthesis, and since then this field has been left to him.

Instead of synthesising glycerol it is obviously equally useful if a fat can be made to yield its glycerol without thereby destroying its edibility. Professor Lapworth and Mrs. L. Pearson found that when olive oil was heated with manitol in the presence of small amounts of sodium ethylate the glycerol could be removed as such, and the residue consisted of a manitol fat similar in all respects to olive oil, and satisfactory from the physiological point of view as appears from the experiments of Professor W. D. Halliburton, F.R.S., Dr. J. C. Drummond, and Dr. R. K. Cannan. The chemical nature of the manitol fat has been carefully investigated and the chief constituent is a mannitan dioleate. This process is simple and

convenient, and in time of emergency might be of considerable importance. Its practicability depends very much on the supply of manitol, though any non-toxic polyhydroxylic substance could probably be used. Professor J. C. Irvine and Miss H. Gilchrist are carrying the matter further. Their original scheme of work included the examination of the synthetic fat obtained by the condensation of manitol with olive oil, and a parallel research in which an easily accessible sugar derivative was used in place of manitol. Professor Lapworth's observations were fully confirmed, and, in order to gain a clearer insight into the reactions involved and the structure of these synthetic fats, a systematic research was commenced on the representative obtained when methylglucoside is heated with olive oil. From the time that the work in question became less urgent (November, 1918) it has been possible to make this study thorough and exhaustive. Sufficient information has been accumulated to show that the reaction is by no means so simple as was anticipated. The main product is an anhydromethylglucoside dioleate, and the properties of this compound have been fully examined in order to ascertain the position both of the anhydride linking and the oleyl residues. It is evident that oleyl chains are liable to undergo further reactions of some complexity, and this naturally affects the behaviour of the compounds on hydrolysis. The results obtained are in the highest degree interesting, and when the investigations are complete, they will furnish an important contribution to the study of carbohydrate fats.

The object of the work on linseed oil carried on under Dr. Robinson was to prepare an edible oil from the material, and only partial success has been achieved. Crude linseed oil may be rendered almost tasteless and odourless by treatment with charcoal, filtration and passing of superheated steam followed by washing with alkali but the unpleasant and characteristic taste develops in the mouth especially in fresh air. Undoubtedly this is due to oxidation and attention was therefore directed at first to the mechanism of this oxidation in order to determine whether or no it can be prevented. The only theory which gave any hope was that the oxidation occurs only in the presence of catalysts and undoubtedly the process is much accelerated not only by catalysts such as the oxides of lead but also by aldehydes. After an exhaustive (so far as was reasonable) series of experiments, however, the conclusion was reached that linseed oil will oxidise *per se*. For example, aldehydes and ketones may be completely removed, *e.g.*, by washing with many changes of sodium bisulphite or a solution of phenylhydrazine sulphonic acid without affecting the drying of the oil. Mr. L. Keffler carried out most of these experiments and found that oil which had been distilled in steam oxidised distinctly less rapidly than untreated oil, but in no case could the oxidation be prevented. It is highly probable that it is linolenic derivatives which start the oxidation process and that the products assist the attack on the less unsaturated constituents of the oil. This is indicated by the increasing speed of the reaction as it proceeds. It was therefore thought that partially reduced linseed oils might not be readily oxidised by atmospheric oxygen and would not be drying oils. A number of partially hydrogenated linseed oils

of varying iodine values were kindly prepared by Messrs. Lever Brothers in an experimental hydrogenating plant, but an unfortunate feature was noticed on inspection of these samples, namely, that a reduced mixture with an iodine value far higher than that of olive oil is semi-solid at the ordinary temperature. The most favourable results were obtained with the hydrogenated oils having iodine values of 96 and 92 respectively and especially with the latter. The oils were centrifuged and separated into a solid and liquid portion. The liquid portion contained no linolenic derivatives, although a considerable proportion of linolic glycerides must have been present. The oil from 92 behaves on oxidation as a good quality olive oil, and it was hoped therefore, that it could be deodorised and used for edible purposes. Unfortunately it was not found possible entirely to remove the characteristic linseed taste, although ordinary methods of refining very much diminish it, and better results would certainly be obtained on a larger scale. The unsaturated acids in the oil have been and are still being investigated. They have been converted into methyl esters and the latter fractionated and crystallised. The work is not yet complete, but so far as it has gone the results confirm the constitution now assigned to linolic acid since both oleic and the expected Δ^8 (12, 13) oleic acid appear to be present. The solid part of the partially reduced oils consists of tristearin mixed with some unsaturated fat from which the tristearin cannot be separated by crystallisation from low-boiling petroleum ether. After five crystallisations the iodine value of the mixture is not altered by further purification. This unsaturated acid has been separated but not obtained in sufficient quantity for identification. On reduction by the Skita method it yields stearic acid. This work is being continued and it is hoped will shortly be ready for publication.

A research on the chemistry of fats synthesised by micro-organisms has been commenced by Dr. Ida Smedley MacLean with the assistance of Miss E. Thomas. The investigation of yeast fat has shown that it is characterised by a high iodine value, in some cases approaching that of linseed oil, and contains a considerable proportion of cholesterol and unsaponifiable matter. The fatty acids present are chiefly linolic and oleic with some palmitic and lauric acids. The presence of the acid $C_{17}H_{33}O_2$ described in the literature and not known to occur in any other fat has not been confirmed.

Bokerny described an increase of fat from 2 to 12.5 per cent in the dried yeast by growing yeast in presence of 5 per cent phenol. This has not yet been confirmed. Bokerny appears to have been misled by errors of method and by investigation of too small a quantity of material.

The addition of even 0.01 per cent phenol to the culture medium appears to hinder the production of fat.

The quantity and nature of the fat present are subject to marked alterations with changes in conditions such as the rate of growth and the aeration of the medium. These changes are now being studied and promise to throw some light on the steps occurring in the production and metabolism of fat.

An important monograph of the unsaturated monobasic acids related to fats has been completed

by the Rev. F. H. Gornall and will be published shortly.

Canned Food Committee.

This Committee, which was constituted but had not begun work when the Report of the Board for 1918 was written, has been actively engaged upon a programme of research the actual prosecution of which is in the hands of Dr. W. G. Savage, Medical Officer of Health to the Somerset County Council. By the courtesy of that Body a room in their Health Department at Weston-super-Mare was placed at the disposal of the Board and was fitted up for the work of the Committee. Dr. Savage has been assisted in his enquiries by Mr. R. Calder and Mr. R. F. Hunwicke.

At the request of the Committee, Dr. Savage visited Canada and the United States during the summer of 1919 to obtain first-hand information as to methods of canning in use in those countries.

The work during the past year has been in the main bacteriological and has been directed towards a critical evaluation of the methods of inspection of tins. A report on this subject has been completed and will shortly appear as Special Report No. 3 of the Food Investigation Board.

A special investigation of the chemistry of the "ripening" of canned fish has been started by Mr. F. W. Foreman and Miss M. Marrack at Cambridge.

Chemistry of Foods and Cooking Committee.

In continuation of work which was begun during the war, by the Chemistry of Foods and Cooking Committee of the Department, experiments have been made by Miss P. Garbutt, under the direction of Dr. C. K. Tinkler, at King's College for Women, on the loss of nutritive material from vegetables in the process of cooking.

W. B. HARDY, *Director.*

*Publications.**

- Ione H. Green, "Report and Experiments on the Cold Storage of Herrings," *Journal of Hygiene*, 1920, xix., No. 1.
- "Interim Report on Methods of Freezing Fish, with Special Reference to the Handling of Large Quantities in Gluts." Special Report No. 4 of the Food Investigation Board. (*In the Press*).†
- W. Stiles, "The Penetration of Electrolytes into Gels," *Biochemical Journal*, 1920, xiv., 58.
- L. F. Newman, "Some Feeding Experiments with Dried Blood," *Journal of the Ministry of Agriculture*, 1920, xxvii., 266.
- F. W. Foreman, "Rapid Volumetric Methods for the Estimation of Amino-Acids, Organic Acids, and Organic Bases," *Biochemical Journal*, 1920, xiv., 451.
- G. S. Graham Smith, "The Behaviour of Bacteria in Fluids as indicated by Daily Estimates of the numbers of Living Organisms," *Journal of Hygiene*. (*In the Press*).

*Note.—A limited number of copies of the papers in scientific journals mentioned in the bibliography which appears in the text are issued as Scientific Memoirs of the Board. Applications for copies should be sent direct to the Secretary of the Food Investigation Board.

†To be obtained (when published) from His Majesty's Stationery Office.

- "On the Design of Railway Wagons for the Carriage of Perishable Foods." Special Report No. 1 of the Food Investigation Board.*
- "The Literature of Refrigeration." Special Report No. 2 of the Food Investigation Board.*
- Franklin Kidd, "Laboratory Experiments on the Sprouting of Potatoes in Various Gas Mixtures," *New Phytologist*, 1919, xviii., No. 8.
- Muriel Wheldale Onslow, "Oxidising Enzymes," *Biochemical Journal*, 1919, xiii., No. 1.
- Dorothy Haynes, "Electrical Conductivity as a Measure of the Content of Electrolytes of Vegetable Saps," *Biochemical Journal*, 1919, xiii., 111.
- Dorothy Haynes and Hilda M. Judd, "The Effect of Methods of Extraction on the Composition of Expressed Apple Juice and the Determination of the Sampling Error of such Juices," *Biochemical Journal*, 1919, xiii., 272.
- Hilda M. Judd, "Iodometric Estimation of Sugars," *Biochemical Journal*, 1920, xiv., 255.
- S. B. Schryver and C. C. Wood, "A New Method for the Estimation of Methyl Alcohol," *The Analyst*, 1920, xlv., 164.
- "Direct Replacement of Glycerol in Fats by Higher Polyhydric Alcohols":—
Part I., Lapworth and Pearson, *Biochem. Journal*, 1919, xiii., 297.
Part II., Halliburton, Drummond, and Cannan, *ibid.*, 1919, 301.
- I. Smedley Maclean and E. Thomas, "The Nature of Yeast Fat," *Biochemical Journal*, 1920, xiv., 483.
- W. G. Savage, M.D., "The Methods used for the Inspection of Canned Foods and their Reliability for this purpose," Special Report No. 3 of the Food Investigation Board. (*In the Press*).†
- "An Investigation of the Methods Employed for Cooking Vegetables, with Special Reference to the Losses Incurred":—
Part I., Helen Masters, *Biochemical Jour.*, 1918, xii., 231.
Part II., Helen Masters and Phyllis Garbutt, *ibid.*, 1920, xiv.

PRODUCTION OF GLYCERIN FROM SUGAR.

At the beginning of the war, Germany was "swimming in sugar," to use a newspaper expression. Production had been greater than ever; large quantities left from the previous years were still available; and exportation had stopped. One of the ten "war commandments" set forth on bills posted in all railway stations, advised the people: "Use plenty of sugar with your meals; sugar is an excellent food." Certain measures of the Government, however, soon made it impossible for the people to follow that advice, and sugar became scarce in the market, although it was known that stocks were plentiful, for the production of the 1913-14 crop had yielded 2,715,870 metric tons of sugar. Germany had been the lead sugar-producing country of Europe, and yet

the people suffered from scarcity of sugar during the war, and were compelled to use honey and saccharin as substitutes. It was supposed that owing to the shortage of fats the Government was trying to conserve the stocks of sugar. However, according to a memorandum prepared by the Research Division of the United States Bureau of Foreign and Domestic Commerce, it now appears that large quantities of sugar which had been withdrawn from human consumption were used in the manufacture of glycerin for war purposes.

The consumption of glycerin in the manufacture of cosmetics and for other purposes, chiefly in the manufacture of explosives, increased enormously during the war, while the supply of the raw materials—fats—was constantly diminishing. It was therefore, necessary to seek other sources, and sugar was selected, as its chemical structure is somewhat similar to that of glycerin. The transformation of sugar into glycerine was accomplished by the biochemical method. It had been known for a long time that in the ordinary fermentation of sugar with yeast small quantities of glycerin would be produced, amounting to about 3 per cent of the sugar. By adding alkalis to the liquid in fermentation the production of glycerin was increased. It was found that almost any salt with an alkaline reaction could be used for that purpose. Experiments were made with acetate, bicarbonate, and dibasic phosphate of sodium, and with carbonate of ammonia. The yield of glycerin was increased to 12.7 per cent, but the alkaline mash was found to be an excellent breeding place for all kinds of acid-forming bacteria, which would pollute the glycerin. This fault was remedied by the use of sodium sulphite, which acts as a poison to the bacteria of lactic acid and others, but does not, even in large quantities, affect the yeast cells (*Saccharomyces*). When sodium sulphite was employed as an antiseptic the yield of glycerin was increased proportionately to as much as 23 to 36.7 per cent of the sugar.

The ordinary fermentation produces not only alcohol, carbonic acid, and glycerin, but also small quantities of acetaldehyde. When the sulphite is added in increasing quantities the yield of acetaldehyde and glycerin increases, while that of alcohol and carbonic acid decreases. The acetaldehyde was used largely for war purposes. The production of glycerin from sugar had a great practical value in war time, according to German writers. The manufacturing process, patented in 1915, was exploited on a large scale, and the production of glycerin exceeded 2,200,000 pounds a month. The invention also possesses an unusual theoretical interest, as it shows how the transformation of materials by bacteria can be influenced by the addition of chemicals. In the words of a German writer, "the biochemical processes open up new prospects for the future, and seem to be destined to provide many substitutes to a people robbed of all raw materials."

Attempts made during the war in Austria-Hungary to produce glycerin from sugar do not seem to have met the success claimed for similar attempts in Germany. Complaint was made by the Bohemian journals of Prague that carloads of sugar had been wasted in recovering negligible quantities of glycerin, and doubts were expressed whether such waste of food could be justified even by the exigencies of war.—*Journal of the Royal Society of Arts*, October 15, 1920.

*To be obtained from His Majesty's Stationery Office.

†To be obtained (when published) from His Majesty's Stationery Office.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 11, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE following papers were read:—

"Calcification of the Vertebral Centra in Sharks and Rays." By W. G. RIDEWOOD, D.Sc.

The patterns presented by the calcified lamellæ of the centra were by Carl Hasse claimed to have an important taxonomic value, and they were employed by him as the basis of his classification in the monograph, "Das natürliche System der Elasmobranchier," published in 1870-1885. The present investigation was undertaken to test the validity of the thesis, and the results go to show that Hasse misinterpreted the facts to a considerable extent, and that his conceptions of "asterospondyly" and "tectospondyly" are unsound.

In the course of the inquiry, 150 sharks and rays, belonging to 68 species and 44 genera, were examined. The investigation largely resolved itself into ascertaining the limits of the three component cartilages of the definitive centrum, namely, the sheath-cartilage, the arch-cartilage, and the perichondrially produced cartilage, and studying the relations of the calcified lamellæ to these parts.

Similarity in pattern of the calcified lamellæ is shown in certain cases to be homoplastic, the lamellæ, although having the same disposition, radial or concentric as the case may be, being developed in sheath-cartilage in some genera and in perichondrial cartilage in others. In some cases the similarity may be accounted for by convergent degeneration from ancestral types which there is reason to believe were themselves different in their mode of calcification.

One of the main conclusions arrived at is that the distribution and proportions of the three kinds of cartilage composing the centrum are of greater morphological importance than the disposition of the calcified lamellæ in them. Another conclusion is that the difference between chorda-centra and arco-centra is relative rather than absolute. In some cases (Lamnidae) the centra possesses so little sheath-cartilage that they approach the arco-centra of *Esox* and *Amia*.

"Studies in the Mechanism of Enzyme Action." By A. COMPTON, D.Sc.*"Effect of Certain Dietary Deficiencies on the Suprarenal Glands."* By C. H. KELLAWAY.

This work was carried out for the purpose of throwing further light on the important observations recently made by McCarrison, concerning the increase in size and in content of adrenalin of the suprarenals of pigeons fed on polished rice.

These changes in the suprarenal glands of pigeons were found constantly when the diet consisted of polished rice alone, or when an adequate ration of protein (casein rendered free from fat and from accessory factors by repeated extraction with alcohol and ether), or fat was added to the dietary, and were associated with the appearance of polyneuritis. The daily administration of a sufficient amount of "Marmite" to the diet of

polished rice prevented these changes from occurring.

An attempt was made to explain the enlargement of the adrenals as being due partly to congestion and œdema of the gland tissues, and partly to the storage in the cortex of the gland of lipoids set free by the breaking down of body tissues, which occurs in birds fed on diets deficient in Water Soluble B. The investigation of the cholesterol content of the adrenals of normal and polyneuritic birds did not support this theory of lipid storage.

The increased residual content of adrenalin was attributed to diminished output of adrenalin, as a result of the greatly lowered metabolism in birds fed on deficiency diets. The histological appearances of the glands suggested obstruction of the venous outflow from the medulla by cortical hypertrophy as an additional cause.

Edema in birds fed on deficient diets was of infrequent occurrence, and could not be produced by the daily administration of large doses of adrenalin. It does not appear to be causally related to increased output of adrenalin. This view is in harmony with the more recently expressed views of McCarrison.

"Genetics of Sex in Funaria hygrometrica." By E. J. COLLINS.

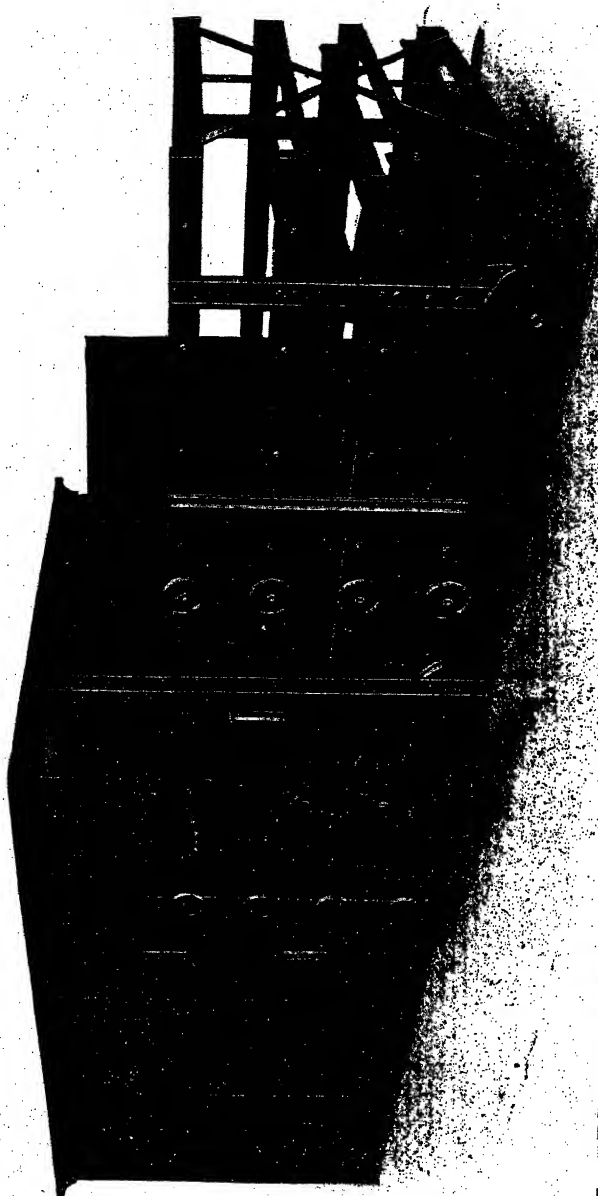
Experimenting with *Funaria hygrometrica*—a monœcious type of moss—it was found that, whilst cultures from spores reproduced the normal monœcious plants, vegetative cultures derived from the antheridia and the surrounding "perigonal" leaves of the male "inflorescence" produced male plants only, pointing to the probability that at some point in the cell divisions by which the axis and its organs are developed, a separation takes place such that the element upon which the monœcious condition depends is dropped out of those cells from which the male organ with its surrounding leaves is formed.

Vegetative cultures from the archegonium and the surrounding "perichætal" leaves have now been made and these have produced typical monœcious plants. The conclusion is that up to the point of the formation of the female organ the cells of the haploid gametophytic phase retain the power to produce monœcious plants, whereas the leaves surrounding the male organ have lost this power. It must therefore be inferred that sex-segregation here occurs in a haploid tissue.

The cytological aspect of the phenomena is not studied, and the generally accepted alternation of generation within the group with its n and $2n$ phases is assumed throughout.

THE NITROGEN AND PHOSPHORIC ACID OF WHEAT.—It was already noted by Messrs. Rousseau and Sirot that in the most suitable flour for bread the proportion of soluble nitrogen is about constant in relation to the total nitrogen. Analyses were made with wheat itself, the samples of grain being taken every five days in the same field. They demonstrated that wheat reaches complete maturity in a state of stability which for nitrogenous and phosphatic matter corresponds to a certain ratio between the soluble and insoluble elements. With different ratios there is a corresponding insufficiency of maturity or a tendency to germination.—*Comptes Rendus*, September, 1920.

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FURTHER PARTICULARS ON APPLICATION.

MEETINGS FOR THE WEEK.

Monday, November 29.

Royal Society of Arts, 8.

Tuesday, November 30.

Society of Chemical Industry. (At Glasgow).
Royal Society, 4. (Anniversary).

Wednesday, December 1.

Conjoint Board, 3.

Royal Society of Arts, 4.30.

Society of Public Analysts, 8. "Estimation of Theobromine" by

Raymond V. Wadsworth.

"A new process for the Estimation of small quantities of

Chromium in Steels" by B. S. Evans, M.B.E.

"Some notes on the reactions between Fulminate of Mercury

and Sodium Hyposulphite" by P. V. Dupré, M.B.E., and

F. H. Dupré.

Thursday, December 2.

Chemical Society, 8.

Friday, December 3.

Society of Chemical Industry. (Meetings at Manchester, Bristol

and Cardiff).

NOTICES.

EDITORIAL.—All Literary communications and Books, Chemical

Apparatus, &c., for review or notice to be addressed to the

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3164.

STREATFEILD MEMORIAL LECTURE.*

By J. H. COSTE, F.I.C.

WATER found in nature is never pure. It contains something not water which forms bubbles on the sides of the containing vessel when the temperature is raised rather rapidly as well as encrusting solids which separate later. This observation must have been made very early; certainly soon after glass vessels were used for heating. It was not, however, until Cavendish had shown how to manipulate gases that the study of such a subject was possible.

The discovery of Henry in 1803 that "under equal circumstances of temperature water takes up, in all cases, the same volume of condensed gas as of gas under ordinary pressure," was followed immediately by Dalton's further generalisation that from a mixture of gases an amount of each gas is dissolved dependent upon the specific solubility of the gas and its partial pressure in the mixture. Dalton gave the following example from his own work—Atmospheric air, consisting of 79 parts of azotic gas and 21 parts of oxygenous gas per cent.

Water absorbs $1/64$ of $79/100$ azotic gas = 1.234 .

Water absorbs $1/27$ of $21/100$ oxygenous gas = 0.778 .

Showing that he had a fair but not very exact knowledge of the solubility of the gases of air in water. He also sought to establish a simple atomic packing of the gas and water atoms of his new atomic theory using a shot piling analogy and diagrams in three dimensional space.

For half-a-century work on the gases in water seems to have been confined to sporadic observations. The methods of investigation available were neither exact or unsuitable for the work which was attempted. This was mostly undertaken afloat in connection with various expeditions sent out by England and France to explore the surface and depths of the ocean. By this means a certain amount of useful information was obtained and published, but an experimental study of the solubility of gases in water and other liquids and of the kinetics of interaction was needed if the subject was really to be advanced. Bunsen, who had brought the methods of gas manipulation to much greater perfection than Cavendish had left them, investigated in 1855 the solubility of many gases in water and other liquids.

It had been generally realised that water freed from air and then exposed to or even shaken with air required a rather long period to reach saturation, although the amount of air taken up was very small, but the first suggestion as to the course of this process seems to have been made by Dittmar. In his report on the physical and chemical work of the great *Challenger* Expedition, published in 1884, he wrote: "Supposing a certain portion of the ocean were separated from the rest, and after some had been deprived of its

gaseous contents, exposed to the air at a constant temperature of t° , the three gases would stream into the water at a steadily diminishing rate until absorptiometric equilibrium was established, *i.e.*, a point reached when, for instance, the number of molecules of oxygen dissolved in a given small time would be exactly compensated by the same number of previously dissolved oxygen molecules returned to the atmosphere." The *Challenger* reports were issued in a vast number of folio volumes, and I suppose few chemists or physicists could afford to buy them. Besides, the investigation of the velocity of chemical reaction was not at that time an attractive subject to chemists.

All work on the rate of absorption or escape of gas from water, from whatever point of view undertaken, leads to the same conclusion, namely, that the reaction between a liquid and a gas followed the same course as that between other heterogeneous phases which have been investigated. We may consider the case of a gas over perfectly still water. The surface rapidly becomes saturated; in fact, there is good reason for considering the surface interchange to be instantaneous, but the downward diffusion of the gas in the liquid is slow and proceeds with greater slowness as the depths are reached owing to the decreasing pressure due to the retention of gas in the upper layers of the liquid. Nevertheless, a continual entry at the surface and procession downwards occurs until the whole of the liquid is saturated with the gas. This case can be treated by means of the application of Fourier's theorem, which is known as Fick's law of diffusion. It has been investigated in the United States by Black and Earle Phelps, but as Adeney and Becker have very recently pointed out, it is most difficult to realise in practice and seldom or never occurs in any actual case needing investigation. The diffusion is extremely slow, and unlike most cases of diffusion of concentrated solution, is not aided appreciably by differences of density, as these seem to be inappreciable. I have not been able on looking at the available data to decide whether water saturated with air is denser or lighter than pure water.

The very slow diffusion can, however, be supplemented by mechanical agitation, in which case the water can be considered as divided into two layers, an upper one where the concentration gradient falls off from saturation at the surface to some lower concentration which is uniform throughout the lower part of the liquid. With increasing rate of agitation the layer of varying concentration becomes thinner and thinner, that is the liquid is uniformly mixed.

The rate of solution of a solid in a liquid was first investigated by Bogusky for marble dissolving in acids and later by Noyes and Whitney and Nernst and Brunner for various not very soluble substances, *e.g.*, benzoic acid. It is an analogous case to that which we are considering, and all workers on the absorption of gases by water, or the escaped gases from water, have found an expression based on Newton's law of cooling to hold good. The rate of absorption

$$\frac{dx}{dt} = k(C - x)$$

where C represents the concentration of full saturation and x the concentration at any moment t ,

*Delivered at Finsbury Technical College, October 14, 1920.

1 cc. of Water Dissolves

	0°	5°	10°	15°	20°	25°
Nitrogen (Bohr and Bock)	0.024	0.043	0.039	0.035	0.031	0.029
Oxygen (Bohr and Bock)	0.049	0.021	0.019	0.018	0.016	0.015
Carbon dioxide (Bohr and Bock)	1.71	1.42	1.19	1.02	0.88	0.76
Argon (Winkler)	0.05	—	0.04	—	0.03	—

K being a constant dependent upon the area of common surface of gas (or solid) and liquid, the nature of the gas (or solid) being dissolved, and the rate of mixing. The law can be expressed also as

$$\frac{c-x}{c} = Kt \quad \text{or} \quad -\log \frac{c-x}{c} = Kt$$

When reduced to unit area the constant K becomes the evasion coefficient β of Bohr, or f the coefficient of escape of Adeney and Becker. These authors, who have studied respectively the rate of escape of carbon dioxide from solution and the rate of absorption of the gases of the air in water, have assumed that they obtain complete mixing and have assigned definite values to β or f . I think that a study of the effect of varying the rate of agitation is necessary before limiting values can be assigned to the evasion constants of gases.

This work on the rate of absorption cannot be properly treated in a rapid survey, but it is of the greatest value in that it indicates that true significance of any observed concentration, *e.g.*, of dissolved oxygen in the water of a stream or even of a lake or pond. Given motion of the water, such as will occur in a tidal or fairly rapid river, the rate of absorption of gases from the air is directly proportional to the saturation difference, as Brunner calls it. In other words, the difference between 100 and the observed percentage saturation with, say, oxygen, is a direct measure of the rate at which the water is, at the time of experiment, absorbing oxygen from the air as compared with the limiting rate. This is exactly what is required to be known in all work on river pollution, and it was the need of this information which led Dibdin to undertake his little-known work on the subject in 1894, which he boldly applied to the solution of his problem of the Thames.

We see that there is a limit to the solubility of a gas in water; that is, for every set of conditions a point is reached when the water will absorb no more gas. It is clearly necessary to ascertain that point for varying conditions. The effect of gas pressure was studied by Henry and Dalton. The other determining factors are temperature and the presence of other matters—such as the salts of sea-water—already dissolved in the water. Water will dissolve more gas at its freezing point than at any other temperature. All the gases as well as other solutes separate on freezing.

The solubility of gases of air in water has, since Bunsen's work in 1855, been determined by many workers whose results are on the whole very consistent. The effect of salts in reducing solubility of gases is well shown in the case of sea water.

For the actual determination, two classes of methods are available; either (1) measured quantities of gas and liquid are agitated at a constant temperature and the decrease of the gas phase noted from time to time until the mass of the residual undissolved gas is constant, whence the

mass dissolved in the water at the observed temperature and pressure can be deduced; or (2) the water is saturated with the gas and the resulting saturated solution is examined as to its content of gas. The former or absorptiometric method as usually applied is suitable only for pure gases, the analytical method is applicable to mixtures such as air.

A slide was exhibited showing the apparatus used by Adeney and Becker for the absorptiometric determination of the gases in distilled and sea water. It may be taken as a type of such apparatus but possess the novel feature of utilising the surface tension of the water for obtaining a bubble of constant surface and volume which also acts as a stirrer.

It is usual, following Bunsen, to reduce the results of determination of solubility of gases to the volume of gas at a pressure of 760 mm.—that is the gas itself, not gas plus water vapour—which one cubic centimetre of water would dissolve at the temperature of experiment. A few such values are given in the table. This value is usually styled the absorptiometric coefficient a .

Since air contains only 78 per cent of nitrogen, 1 per cent of argon, and 21 per cent of oxygen, with about 0.03 per cent of carbon dioxide the amounts of these gases dissolved from it are reduced from those given proportionated to these amounts, and since also air over water is always saturated with water vapour—at least at the interface—which as we have seen is the locus of the mutual action, the amounts are further reduced from this cause, a fact which is not always remembered.

One very convenient result of this is the fact that water dissolves from air just about one-half as much oxygen as nitrogen, so that one gas is a simple measure of the other. This ratio is not maintained throughout the whole range of the temperature from 0° to 100° C., but Tornøe showed that the proportion of oxygen decreased more rapidly than that of nitrogen as the temperature rose, and Winkler deduced the following equation:—

$$\left. \begin{array}{l} \text{Percentage of oxygen in} \\ \text{air boiled out from water} \end{array} \right\} = 35.47 - 0.0338t$$

showing that the limiting percentages between 0 and 100 are 35.47 and 32.09, or ratios of oxygen to nitrogen plus argon 1:1.82 and 1:2.11.

The curve showing the solubility of atmospheric oxygen in water from 0–100 has been calculated from Winkler's tables for an observed pressure of air plus water vapour of 760 mm., hence the zero value at 100.

The volumes of gases dissolved are not large when considered as volume per volume, but the weights of gases dissolved are very small indeed. For example, distilled water which is fully saturated with air at 15° C. and normal barometric pressure, contains only one part per hundred thousand of oxygen—0.001 per cent.

Ordinary river water would dissolve as much, but sea water only contains about 80 per cent of this amount—0.0008 per cent. Yet, as we shall see later, these very small concentrations have far-reaching effects on some of the properties of water.

The absorptiometric method is useful as a means of determining the solubility of a gas in water, but we need an analytical method by which the actual amount of gas dissolved in any water can be determined.

A sample of water must first be obtained which has not been exposed unnecessarily to the air. The process of filling a bottle in the ordinary way will obviously tend to aerate the water which is collected.

This can be avoided by using a canister which contains a bottle of much smaller capacity. Water entering through a central tube fills the bottle which overflows, a current of water passing through it until the canister is full. The air in the system escapes at the side tube and the bottle finally contains water which has not been in contact with air.

The oxygen and nitrogen in water can easily be removed by boiling, as is being done in the large flask which some here will remember having seen Mr. Streatfeild use in the laboratory. It is impossible to remove all carbon dioxide by this means, except by making the water acid and boiling for rather a long time. The method was used by Bunsen, who got over the difficulty of loss of water by expansion and of gas by solution in condensed water, by using a gas-collecting tube above the flask of water, which tube he separated by tying the rubber connection and then boiled out the air and sealed the top, afterwards removing the ligature and boiling the water to be examined, so that the gases all collected in the tube, which could be disconnected. Jacobson improved on this by substituting for the ligatured rubber tube a tube with a side hole, which, after the collecting tube was freed from air and sealed, could be pushed down into the water to be examined, which was then boiled and the gas collected and sealed off. This apparatus was used by Buchanan on the *Challenger*. It must have required much skill to use on a small but lively vessel. Several useful pumping out methods have been used, e.g., by MacLeod, Dibdin, and Adeney, but it is desirable to avoid contact of mercury with the water to be examined, or loss of oxygen may occur.

The most practical gasometric method for oxygen and nitrogen is Winkler's. The gases are evolved in a stream of CO_2 generated from calcite by hydrochloric acid in the measuring vessel and collected over potash solution in a graduated tube, in which they are measured, and the oxygen absorbed by "pyro." This can easily be used on a steady ship and could be arranged for using on a lively one.

Oxygen, from its great chemical activity, can be determined by chemical means. Of many methods the best is certainly Winkler's manganese process, which is well known. Carbon dioxide may be determined by the usual method of titration of the base combined with it by acid and methyl orange and of the free and bicarbonate CO_2 by sodium carbonate and phenol-phthalein. Another method which is applicable to a long series of determinations is by comparing the tint produced in the water in question by such indications of alkalinity with those produced in a

series of "buffer mixtures." Mixtures of boric acid and borax, mono- and di-hydrogen alkali phosphates, or other salts of weak di- or tribasic acids, may be used. The carbonate acid bicarbonate, bicarbonate-carbonate equilibrium, has been studied by Prideaux and the alkalinity of such mixtures is well defined. The experiment of passing carbonic acid into a very dilute solution of sodium carbonate coloured purple with a mixture of α -naphthol phthalein and phenolphthalein will illustrate the effect of an increasing proportion of acid to base. First the crimson colour imparted to phenol-phthalein will disappear as the liquid becomes less alkaline by absorption of carbon dioxide, then the blue of α -naphthol phthalein which continues until the point of absolute neutrality is nearly reached. We may now add a neutral point indicator such as neutral red, and until the gradual reddening as the concentration of carbonic acid increases. The reverse series of changes will occur if air is blown through the acid solution.

What, if any, is the significance of all this to anyone but the physical chemist? This is, of course, a vulgarly materialistic question, but such questions are asked.

It is a noteworthy fact that many of the people who have investigated this matter have not been at all interested in physical chemistry, but rather in oceanography, marine biology, public health, or engineering, and have struggled with a subject which fell necessity forced them to study as best they could.

All the animals of the sea and rivers except warm-blooded air-breathing ones have to depend upon the oxygen dissolved in the water for respiration and are able to pump into their gills a sufficiency of water for this purpose. Hoppe Seyler and Duncan, and more recently Addyman Gardner, have examined the respiratory requirements of a variety of fishes which as they have no definite body temperatures to keep up are much less than those of land animals. Gardner found that the respiratory quotient of brown trout went up so rapidly with rising temperature that the fish becomes incapable of sufficient muscular effort to force the required amount of water through its gills. It will be remembered that the amount of oxygen available in the water, unfortunately for the fish, decreases rapidly with the rising temperature. This explains the distress of fish in shallow water during very hot weather. Conversely, respiration slows down to hibernation point at low temperature. The rather high oxygen requirement of the Salmonidæ generally accounts for the inability of salmon to frequent the Thames, where they would, in their migration to and from the sea, encounter a zone of very low aeration than they could tolerate in the region of the sewage outfalls.

Natural water is not entirely dependent upon the air for its dissolved oxygen. It is well known that vegetable life in water will enable it to support a larger population of fish. Owing to the ability of green plants under the influence of sunlight to take up the carbon dioxide given off by animals, utilising the carbon for building their tissues and giving out the oxygen which is not needed. I have found enormous excesses of oxygen in water containing plenty of weeds, on a bright warm day—up to 80 per cent excess over saturation. This becomes greater as the day

advances and falls during the night partly by escape into the air and partly because it is spent in oxidising organic matter.

The carbon dioxide also has a very important effect on life in water. Very small difference of hydron concentration due to changes in the carbonate-bicarbonate equilibrium seem to have an important function in determining the migration of various living organisms which if not themselves of economic value are food material for others that are.

A sea without dissolved gases would certainly be a dead sea.

The relative amounts of gases in water are small, yet if we take Sir J. Murray's estimate of the masses of the seas of the globe they should contain about 10 billion tons of dissolved oxygen if approximately separated. The proportion of carbon dioxide is about 98 mgrms. per litre, or in the whole ocean about 120 billion tons. The ocean has been shown by Schloesing to act as a great equaliser of the content of this gas in the atmosphere by reason of its carbonate-bicarbonate system.

Apart from its biological value in conserving higher aquatic life, dissolved oxygen is of importance in maintaining water in a reasonable state of purity, although there are strong reasons for sewage disposal by discharge into streams; but the introduction in a stream of a great mass of oxidisable matter frequently leads to putrefaction and offence. The changes which refuse undergoes in a river are, in sum, similar to those occurring in a dust-destructor—that is, complicated organic compounds are oxidised to stable and inoffensive products. Since they occur at temperatures several hundreds of degrees lower the rate is much less rapid and the intermediate stages are more readily discovered. In both cases a large proportion of oxygen is necessary for the combustion. In the fiery burning oxygen is obtained direct from the air; the mechanism of combustion is less simple than is shown in the usual equations. In a river all the necessary oxygen must first be dissolved, mostly from the air, partly perhaps from plants, and then interact with the organic matter through the agency of living organisms, bacteria, and others.

It frequently happens that through slowness of flow, inadequate volume, or other causes, the rate of absorption of oxygen in a sewage-polluted stream is insufficient for the desired changes to proceed with sufficient rapidity, and the products of incomplete oxidation produce nuisance, as will those from a destructor of faulty construction. In such cases, warning is given beforehand by a decrease in the proportion of dissolved oxygen, which as it is taken up by the polluting matter and the water becomes more unsaturated, can be absorbed from the air at a more rapid rate. If no dissolved oxygen is found in the water on analysis it means that the river has reached the limit of oxygen supply for its then condition of flow. Usually a more or less stable equilibrium is established at some point intermediate between saturation and zero where absorption from the air is balanced by the bio-chemical demand of the oxidisable matter.

Nitrogen and argon dissolved in natural waters appear to be as inert as the name of the latter implies but oxygen and carbon dioxide account for much of the geological change which leads

to the disintegration of rocks and the presence of dissolved salts in the water. The boiling out of carbon dioxide causes a separation of calcium carbonate which gives engineers so much trouble when unsoftened water is used in boilers. These two gases are also responsible for much of the trouble experienced in the corrosion of iron and of lead. This is too large a subject to touch on to-day, but I mention it to show that the gases in water may be harmful as well as beneficial.

Two practical considerations arise out of all this.

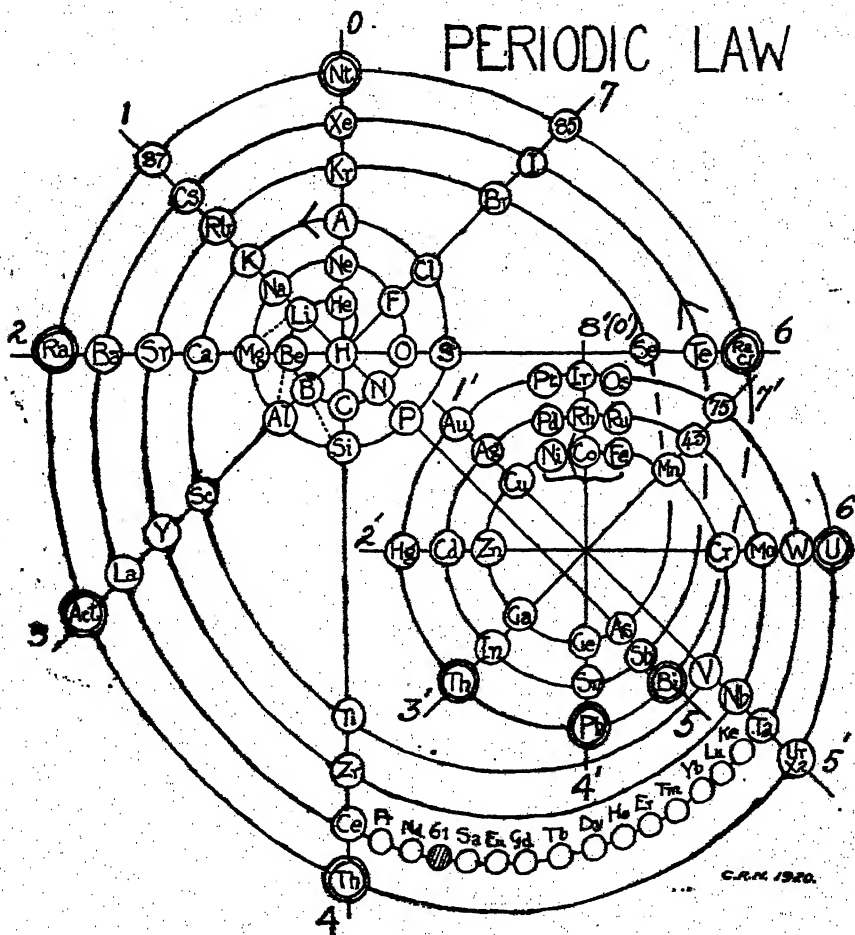
First. It is sometimes desirable to accelerate the process of absorption of gases from the air, usually with a view to oxidation of matters in the liquid. This can be done if practicable—it usually is not—by increasing the air pressure or more easily by increasing the area of the interface. In the most modern processes of sewage treatment this is done rather by passing air through the liquid in very small bubbles, thereby imparting to a relatively small mass of air a large surface (the usual activated sludge method of diffusing tiles) than by increasing tank area. My friend and colleague, Colonel W. Butler, has suggested the inverse process of spraying the mixture of sewage and activated substance through the air. Another method, when area remains constant, is to promote mixing so as to reduce Brunner's layer of concentration gradient to a minimum. This has been successful at Sheffield, where Mr. Haworth has used it for purifying sewage on a very limited area of land.

Second. It is frequently desired, for example, in steam raising to keep out air from water. If air is not already dissolved in the water, the surface of exposure to air if such cannot be avoided, must be kept as small and as undisturbed as possible. The surface temperature may be raised to decrease tension of the air gases and also their solubility and rate of absorption.

If the water already contains air, a rise of temperature or decrease of pressure with increase of surface will aid escape. Condenser water from a steam engine is usually gas free, as it is condensed over a large surface in a partial vacuum. Oxygen can be removed by chemical means. The water of a hot-water pipe system has been found to be oxygen free, with atmospheric nitrogen as a supernatant gas in radiators on the top floor of a large building. This removal of dissolved oxygen by corrosion of iron might be regulated at will by using large anodic surfaces of iron in a feed water system.

It may be noted that in the lungs, in a sewage works, on a metallic surface the most active gas of the air oxygen only becomes active when *dissolved in water*.

THE SPECTRA OF ABSORPTION OF PHOSPHORUS FOR X-RAYS.—Utilising the Siegbahn apparatus with revolving gypsum glass, Mr. Bergengren directed his researches to ammonium phosphate, phosphoric acid, and red commercial phosphorous. The anti-cathode of the bulb was constituted by a tungsten plate, the current not exceeding 80 milliampères under 16,000 volts. The wave length of the limits of absorption are thus different for different varieties of phosphorus and the chemical state of an element has therefore a certain influence on its spectrum of X-rays.—*Comptes Rendus*, September, 1920.



A CONVENIENT FORM OF THE PERIODIC CLASSIFICATION OF THE ELEMENTS.

By C. R. NODDER.

THE accompanying arrangement of the elements, while possessing no essentially novel features, is probably the form in which their natural relationships can best be illustrated without recourse to a three-dimensional arrangement. It is practically Harkins' spiral arrangement adapted for a representation in one plane. In the form of a wall chart it should be a distinct improvement on the usual form for teaching purposes. Corresponding radii of the primary and secondary spirals are parallel to one another and are similarly numbered. In the case of the five missing elements (four of which lie on radii 1, 1', and 7') the atomic numbers are indicated in the circles. The missing rare-earth element of atomic number 61 is the third element after cerium, just as elements

of atomic number 43 and 93 are missing after zirconium and thorium. Neglecting the rare earths, moreover, the third element after cerium is missing. The dotted lines in the diagram will serve to recall the interesting resemblances of lithium and magnesium, beryllium and aluminium, boron and carbon. The double circles are intended to indicate pleiads of isotopes which have been discovered by a study of radioactive transformations. Lastly, barbs have been placed between those elements whose chemical properties require a reversal of the order suggested by their atomic weights.

Cambridge, October 30, 1920.

TECHNICAL INSPECTION ASSOCIATION.—A Paper on "Some Features of Tensile Fractures" will be read by Dr. G. H. Gulliver at the Rooms of the Royal Society of Arts, on Friday, December 10, at 7.30.

SILICA, ITS SEPARATION FROM ALUMINA, &c.

A. METHODS OF DECOMPOSING THE ROCK.

FEW limestones are so pure that they leave no residue on treatment with hydrochloric acid. The residue may consist of quartz, clay, or other silicates, carbonaceous matter, pyrite, &c., and the mode of attack employed will depend on the amount of insoluble matter, and whether or not it is desired to know its composition separately from that of the soluble portion.

a. When the Inorganic Residue is to be Separately Analysed.

A grm. of the rock powder is moistened with water and dissolved in dilute hydrochloric acid (or acetic, if the former acid is likely to act appreciably on the silicates) in a covered beaker till all effervescence ceases. Moderate heat is needed if the effervescence is so weak as to indicate a rock of dolomitic character. The solution is filtered through a 7-cm. filter, and the residue washed with water, or hot dilute hydrochloric acid should gypsum be present and the silicates resistant. The paper, with its contents, is ignited moist in platinum (blast needed only if the amount is considerable), and after weighing it is fused with sodium carbonate and analysed like a silicate rock. If it contains hydrous minerals the original water content of the residue is best determined by a separate test on a fresh portion of the sample and not by drying and weighing on a counterpoised filter and then igniting. The weight of water found should be added to that of the ignited residue in order to get the true weight of the insoluble matter.

If the ignited residue is wholly quartz, or is very insignificant in amount, it may be treated at once with a drop of sulphuric acid and a few drops of hydrofluoric acid, and the acids removed in the radiator. If then a slight residue still is visible, it is well to repeat the treatment with acids and evaporation, for it cannot be too insistently pointed out that quartz resists the action of hydrofluoric acid far more than many silicates, and several evaporations may be needed to volatilise the crystallised mineral unless it has first been reduced to a most impalpable state of division. When the weight after exposure for a few minutes to the full burner heat no longer changes, the loss represents silica. If a slight residue still shows (it is most likely to be mainly alumina), the subsequently obtained precipitate of alumina, &c., is added to it and ignited in the same crucible.

If the original residue is small, and accurate knowledge of its composition is desired, several grms. of the rock may be dissolved. In this case, the whole filtrate from the insoluble matter is best treated for dissolved iron, aluminium, and manganese, but then only an aliquot part of the subsequent filtrate should be used for the determination of calcium and magnesium.

In case the filtrate from the residue is coloured perceptibly by dissolved organic matter, a condition that may arise occasionally, this organic matter must be effectually destroyed before proceeding to the precipitation of iron and aluminium, for otherwise incomplete precipitation of

one or both will be the result. The complete removal of this disturbing material cannot always be effected by ordinary oxidising agents, but only by evaporation and heating to its carbonisation point. In doing this it is necessary, in order to avoid possible loss of iron as chloride, to evaporate with nitric acid to dryness a couple of times and then to heat over a free flame gently till the desired result is achieved. If this seems undesirable for any reason, it may be better to start with a fresh portion of the limestone and to treat it by one of the methods given under *b* below, for the bulk analysis.

b. When the Inorganic Residue is not to be Separately Analysed.

The usual case does not involve separate analysis of the inorganic residue. As said above, the residue may consist of clay or other silicates, carbonaceous matter, pyrite, &c., with or without quartz. There are two ways open to render the noncombustible part of this soluble.

a. By solution in acid after strong ignition.—Solution in acid after strong ignition is the best method to employ if the ratio of insoluble to soluble compounds is not less than that in an argillaceous limestone which is directly suited for burning to Portland cement—that is to say, if the silica does not much exceed 15 per cent and the oxides of iron, aluminium, and titanium together are not in excess of 6 per cent. The exact allowable limits have not yet been determined, nor is it known what the proportions may be in dolomites and dolomitic limestones. This is a subject for further investigation.

Limestones, however, in which the above percentages of silica, alumina, &c., are not exceeded may be converted in 10 to 15 minutes by a good blast capable of giving an effective temperature of 1100° to 1200° to a product that is wholly soluble in hydrochloric acid, provided the rock was first reduced to a very fine powder.

A grm. of the powder is heated in a covered platinum crucible by an inclined blast. If a limestone, the flame may be applied at once, as a rule, without fear of loss, or after short exposure to a full Bunsen flame. Highly magnesian limestones, if this method is applicable to them, must, however, be heated with the greatest caution, for their temperature of decomposition is far below that of limestones, and violent projection of material often begins far short of visible redness.

The strong heating is usually stopped after 10 or 15 minutes, when the shrunken product may have the appearance of a sintered or even clinkered mass that detaches for the most part readily from the crucible. (The changes that take place during the ignition comprise loss of all carbon dioxide, water, and carbonaceous matter; oxidation of all pyrite, with retention of the whole of the sulphur as calcium sulphate. Prolonged heating will gradually expel all the sulphur trioxide from the calcium sulphate and later the alkalis, which can be wholly volatilised in an hour or less by a powerful blast. With an inclined blast the alkalis condense in one part on the under side of the lid as a soluble and powerfully alkaline deposit, sometimes weighing several milligrams, but in the time above set no loss of alkali appears to occur). It is transferred to a beaker or evaporating dish and moistened with

water. The crucible is then cleaned with hydrochloric acid (1:1), and the contents are poured into the beaker or dish. By gentle heat and cautious pressure with the flattened tip of a rod the lump or lumps are caused to disintegrate and pass largely into solution in a few minutes. A certain amount of silica may remain undissolved in a flocculent state, but this of no moment. When all grit has disappeared, the liquid, if in a beaker, is washed into a dish and evaporated to dryness. If solution was made directly in the dish the volume of liquid need not exceed a few cubic centimetres and the evaporation takes but a short time. A much smaller dish is allowable than in the case of wholly siliceous minerals, because of the small bulk of solution and the entire absence of added fixed salts.

B. By solution in acid after heating with sodium carbonate.—When the siliceous components are in such amount as not to permit the formation of a wholly soluble product by strong ignition, it is necessary to mix sodium carbonate with the powder and decompose the silicates by its aid over the blast lamp. This procedure may be adopted with all siliceous limestones if desired. The amount of flux to be used is but a fraction of that needed for a silicate analysis. One-fourth to one-half grm. for 1 grm. of limestone suffices (P. W. Shimer, in R. K. Meade, "The Chemist's Pocket Manual," p. 162), for the lime formed by ignition is itself a powerful flux, and it is quite unnecessary to have here a liquid fusion. A sintering suffices. This proportion holds also for highly magnesian limestones and for cement rocks containing as little as 50 per cent of lime (personal communication from R. K. Meade).

B. SEPARATION OF SILICA.

Because of the absence of large amounts of alkali salt and of much silica and the evaporation of the hydrochloric acid solution obtained in A, *a*, and *b*, *a*, and *b*, takes little time as compared with a silicate analysis. When dry, or nearly so, on the steam bath, the dish may be placed in an air bath or (covered) on a platinum triangle resting on a hot plate, and heated to 200° for an hour if a limestone is under treatment, but for a highly magnesian limestone the temperature should not exceed 120°, according to J. P. Gilbert (*Tech. Quart.*, 1890, iii, 61; Abstract in *Zeitschr. anal. Chemie.*, 1890, xxix, 688) because of recombination of silica and magnesia, with subsequent resolution of the silica when acid is added.

Bertram Blount claims (*Jour. Soc. Chem. Ind.*, 1902, xxi, 1217) that by heating to 200° in this manner the silica is completely separated by a single treatment, but I have not found it so, though the amounts going into solution on subsequent addition of acid are small, seldom over 2 or 3 milligrms. Therefore, for exact work with silica present to the amount of 2 to 4 per cent and over, that already rendered insoluble should be filtered off and the solution again evaporated. With this end in view the dry mass is drenched with strong hydrochloric acid and allowed to stand for a few minutes, then as much water is added and the dish covered and placed on the bath for 10 minutes. Instead of strong acid that of half strength may be used and the heating begun at once. The silica is then separated by filtration on a filter of suitable size, washed

thoroughly with dilute acid and then twice with cold water. The filtrate is evaporated again to dryness, the residue extracted with hydrochloric acid as before, but with allowance of only a few minutes' time and the solution filtered once more through a second and smaller paper. The two papers with their contents are slowly dried, charred, and ignited in platinum, finally over the blast for 10 minutes. The weighed silica is to be corrected for foreign matter by evaporating with 5 cm. (*Jour. Soc. Chem. Ind.*, 1902, xxi, 1217) of hydrofluoric acid and one or two drops of sulphuric acid. The residue obtained after ignition is almost always considerably less than that found in analysing a silicate rock, and an ignition of a minute or two over a full burner, after expulsion of the sulphuric acid, is in almost all cases sufficient. The composition of this residue is similar qualitatively to that derived from silicate rocks. It should never contain calcium or magnesium but consists mainly of alumina, with a little ferric, titanic, and phosphoric oxides. It is preserved, and the subsequently obtained precipitate of these oxides is added to it and ignited in the same crucible.—*Bulletin* 700, N. S. Geological Survey.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 18, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following papers were read:—

"The Absorption and Scattering of Light." By Sir ARTHUR SCHUSTER, F.R.S.

The paper is based on the generally accepted theory that refraction and dispersion are caused by the oscillations of electric resonators embedded in the medium through which the light passes. With homogeneous light each resonator responds with a forced oscillation, together with a motion following the laws of free oscillations, and gradually dying out. If the white light falls on the medium, the forced oscillation has to be replaced by an integral and other terms added that are due to disturbances caused by neighbouring molecules.

The principal result of the paper is that all the terms of the equation are spectroscopically identical. If the proper value for $f(\mu, \omega)$ be introduced, and E regarded as constant, then the integral in the first term of the right-hand side is merely the analytical representation by Fourier's integral of any of the terms of the summation, with a proper adjustment of ϵ and t_s . As it stands it represents a motion beginning at time $t=0$ and continuing according to the laws of a damped oscillator.

The mechanism of scattering and absorption is discussed, and Lord Rayleigh's equation for the coefficient of extinction in a scattering medium is obtained in a more vigorous manner, so as to include cases where $\mu-1$ is not necessarily small.

"*The Emission of Electrons under the Influence of Chemical Action.*" By Prof. O. W. RICHARDSON, F.R.S.

The electron currents to a surrounding metal electrode from spherical drops of the liquid alloy of sodium and potassium under the influence of chemical action with a number of gases have been investigated and measured under various conditions. The gas which has been studied most is phosgene (COCl_2), then, in decreasing order, Cl_2 , H_2O , and HCl .

In all cases the relation between the current and the applied potential difference is of the same general character. When proper allowance is made for the contact potential difference between the two metal surfaces it is found that the electron currents are nearly constant for small accelerating electric fields. Thus, as in the case of photoelectric emission, the saturation value of the current is reached with a potential difference very close to zero. With retarding fields the currents fall off rapidly as the applied potential difference increases. Like similar thermionic electron currents they approach the voltage axis gradually and not sharply as in the photoelectric case.

The true zero on the voltage scale is difficult to determine on account of fluctuations in the contact potential difference. In the case of COCl_2 it has been possible to locate the zero to within 0.10 volt by a photoelectric method.

The proportion of the chemically emitted electrons whose kinetic energy lies between u and $u+du$ is very closely represented by

$$\frac{u du}{kT^2} e^{-u/kT}$$

where k is Boltzmann's constant and T is a certain temperature. For the case of COCl_2 , T is near 3300°K , and for the case of Cl_2 , T is about 4900°K . The formula above represents a Maxwell distribution for the temperature T . Thus the distribution of kinetic energy among the chemically emitted electrons is the same as that among the molecules of a gas at the uniform temperature T .

"*Magnetism and Atomic Structure.—I.*" By A. E. OXLEY, M.A., D.Sc.

This communication is an extension of former papers on "The Influence of Molecular Constitution and Temperature on Magnetic Susceptibility" (*Phil. Trans. Roy. Soc.*, 1914, ccxiv. A; 1915, ccxv. A; 1920, ccxx A). From Tyndall's work and recent experiments of the author on the characteristic deportment of diamagnetic and paramagnetic crystals in the magnetic field, it appears that in non-ionised crystal structures the fundamental unit of the space lattice is the molecule. It is shown that the electron orbits in atoms must be distributed in space round the nucleus, each electron describing a small orbit, or alternatively the electron itself may be a complex unit endowed with magnetic properties. In either case the distribution must be such that the aggregate projected area of the electron orbits on a plane perpendicular to the principal cleavage is a maximum both in diamagnetic and paramagnetic crystals. This result is consistent with a closer packing of the molecules in a direction parallel to the principal cleavage. In crystals of the simple

cubic form, X-ray analysis has indicated that the structure is an ionised-atomic one, and the cleavages are all of equal value. Such crystals show no appreciable structural deportment in the magnetic field.

The above views relating to electron distribution are consistent with the cubical atom theory of Lewis and Langmuir, but not with Bohr's theory. The coupling forces between atoms and molecules in non-ionised crystals are due to the mutual magnetic induction between pairs of electron orbits. A model of the hydrogen molecule is given in which the arrangement of the coupling units determines a diamagnetic molecule as required by experiment.

It is considered that the above views and those of Bohr may eventually be brought into line by a fuller recognition of the possible differences between radiating and non-radiating matter.

"*The Proximity of Atoms in Gaseous Molecules.*" By Prof. A. O. RANKINE.

In this investigation a close examination is made of the relations between the estimates of atomic diameters obtained by W. L. Bragg from X-ray crystal measurements and those deduced from the kinetic theory of gases. The examination is carried out from the point of view of the Lewis-Langmuir molecular theory. It is shown that if, for example, a hypothetical molecule be constructed of two argon atoms with their centres separated by the distance demanded by W. L. Bragg's figures, the behaviour of such molecules in thermal agitation would be almost identical with the actual behaviour of chlorine molecules. Similar relations are shown to exist for the pairs of gases, neon-oxygen, krypton-bromine, and xenon-iodine. The following conclusions are regarded as justified:—

(a) There is substantial *quantitative* agreement between the estimates of atomic dimensions deduced from X-ray crystal measurements and from the kinetic theory of gases.

(b) In size and shape the atoms of the monatomic inert elements are nearly indistinguishable from the atoms, respectively, of the neighbouring diatomic elements in the periodic table.

(c) The Lewis-Langmuir molecular theory accounts satisfactorily for the kinetic behaviour of the molecules of oxygen, chlorine, bromine, and iodine in relation to the behaviour of the corresponding inert atoms, neon, argon, krypton, and xenon.

"*The Similarity between Carbon Dioxide and Nitrous Oxide.*" By Prof. A. O. RANKINE.

The two gases in question have been shown by Langmuir to have almost identical physical properties. In particular, they have the same viscosity, and the application of modern kinetic theory indicates that their molecules have the same size and shape. In the present paper, it is shown, by the extension of methods already described by the author, that the kinetic behaviour of the molecules, both of CO_2 and N_2O , is consistent with their being identical in size and shape with three neon atoms in line and contiguous, *i.e.*, with outer electron shells touching. This is in accordance with Langmuir's view of the constitution of these molecules.

'Forces in Surface Films. Part I.—Theoretical Considerations. Part II.—Experimental Observations and Calculations. Part III.—The Charge on Colloids.' By A. M. WILLIAMS, D.Sc.

Parts I. and II.

1. Attention is directed to the effects of (i) accessibility of surface and (ii) adsorption on the apparent specific volume of finely divided solids.
2. A simple theory of these effects is developed.
3. Observations are in agreement with this theory.
4. The true specific volume of a specimen of charcoal, which appeared to be 0.51 in water and 0.46 in chloroform, was evaluated as 0.67 cc. per grm.
5. The attractive pressure on the surface film on the charcoal was calculated and found to be of the order of 10,000 atmospheres, while the internal pressure of the charcoal itself was evaluated as of the order of 50,000 atmospheres.

Part III.

1. It is shown that compressive forces of the order previously determined may give rise in the adsorption layer to a diffusion potential difference of the magnitude observed in the case of suspensoids.
2. The influence of the diffusion of hydrogen and hydroxyl ions on the potential difference is emphasised, and the neutralisation of the charge on suspensoids and their consequent precipitation explained in terms of diffusion potential.

MINERALOGICAL SOCIETY.

Anniversary Meeting, November 9, 1920.

SIR WILLIAM P. BEALE, Bart., K.C., President,
in the Chair.

"A Graphic Method for the Comparison of Minerals with four variable components forming two isomorphous pairs." By Dr. E. S. SIMPSON.

In the spinel-chromite series the two pairs are MgO.FeO , and $\text{Al}_2\text{O}_3.\text{Cr}_2\text{O}_3$, and the general formula is $(\text{Mg,Fe})\text{O}.\text{(Al,Cr)}_2\text{O}_3$. The relative molecular preponderances of the components of each pair stated as a percentage of the maximum is given by the formulæ $x=100(m-f)/(m+f)$ and $y=100(a-c)/(a+c)$, where m , f , a , c represent the number of molecules of MgO , FeO , Al_2O_3 , Cr_2O_3 , respectively. The values of x and y , calculated from a number of published analyses, and from new analyses of ceylonite from Camban, Western Australia, are plotted on rectangular coordinates. The four corners of the main square are occupied by the pure compounds $\text{MgO.Al}_2\text{O}_3$ (spinel), $\text{FeO.Al}_2\text{O}_3$ (hercynite), $\text{FeO.Cr}_2\text{O}_3$ (chromite), and $\text{MgO.Cr}_2\text{O}_3$ (here named picrochromite). Sub-species and varieties of intermediate composition are divided off in symmetrical areas within the square.

"Fibrolite (=Sillimanite) as a Gem-stone, from Burma and Ceylon." By L. J. SPENCER.

Water-worn, prismatic crystals from the ruby mines in Upper Burma measure up to $1\frac{1}{2}$ cm. in length, and are clear and transparent, with a pale sapphire-blue colour and marked pleochroism. A fine, faceted gem cut from this material is shown in the British Museum collection of minerals. Determinations were given of the optical constants; the birefringence shows a wide range, $\gamma-a$ being seventeen times $\beta-a$. On a somewhat similar, but etched, crystal from Ceylon the axial ratios were determined. Other crystals from Ceylon are pale greyish-green with a marked chatoyancy.

"The Origin of the Alkali Rocks." By Dr. J. W. EVANS.

The alkali-igneous rocks form an exceptional series varying in composition from acid to basic characterised by a high percentage of alkalies, especially soda, and a deficiency in alumina and the oxides of the divalent elements. They appear to occur mainly in areas where the earth's crust has, as the result of ancient folding or the accumulation of granitic rocks, consolidated to a considerable depth, and where the temperature gradient is normally low. Such areas are rarely subject to new folding, but are frequently folded, and with these faults the alkali rocks appear to have a genetic relation. In such areas crystallisation must proceed in the sub-crystal magmas, which are believed to be basic in composition under exceptional pressure, with the result that minerals with low specific volumes, having regard to the materials of which they are composed, will preferentially crystallise out. Garnet, zoisite, fibrolite, and kyanite are examples, the materials of which crystallise out under less pressure with greater specific volumes. As these minerals are mainly silicates of aluminium and the divalent elements, the uncrystallised residue will be poor in these constituents and rich in the alkalies, especially soda, which was present in the original magma in greater proportion than the potash. It will also contain the volatile fluxes in large amount. As a result of the faulting of the crust, this residue may be pressed out, find its way upwards, and give rise by further differentiation to the alkali rocks.

"Monticellite, from a Mixer Slag." By A. F. HALLIMOND.

The crystals, which are essentially monticellite containing about 20 per cent of olivine in solid solution, have the following physical characters: orthorhombic, $a:b:c=0.4382:1:0.5779$; forms 010, 110, 021; refractive indices $n_p 1.663$, $n_g 1.674$, $n_o 1.680$; $2V 73^\circ$; specific gravity 3.20.

"A Refractometer for the Determination of Liquid Mixtures." By Dr. H. H. THOMAS and A. F. HALLIMOND.

A telescope and collimator with Websky signal are fixed in alignment; between them is inserted a parallel-sided trough containing the liquid to be determined, in which is immersed a right-angled prism of known index near that of the liquid. Two images of the signal are formed, and the angular distance between them is read on the eye-piece scale; this reading is proportional to the difference of index between the liquid and the prism. The scale division has the same value whatever the index of the prism used.

CORRESPONDENCE.

NATIONAL PHYSICAL LABORATORY
REPORT FOR 1919.*To the Editor of the Chemical News.*

SIR,—On page 130 of this Report reference is made to the testing and experimental work carried out in connection with the manufacture of balloon fabrics for war purposes, and in connection with same we wish to place on record this Company's work in the manufacture of materials, especially hydrogen-proof fabric for lighter-than-air craft.

The North British Rubber Company first took up the manufacture of this material in 1908, and realising that the problems involved in manufacture necessitated scientific control, as a preliminary, installed in their laboratory an apparatus for measuring the permeability of rubber to hydrogen, and thereafter initiated research into the factors responsible for the deterioration of rubber under the influence of light.

When the Admiralty installed their Test Station at Manchester, we were requested by the officer in charge to furnish drawings of the special type of hydrogen diffusion apparatus which had been designed at Castle Mills, and one of their staff received a course of instruction in the Company's laboratories on the procedure to be followed in testing balloon fabric. At a later period of the war, this Department was taken over by the newly-formed War Office Aircraft Fabrics Department, who installed an extended testing plant, and another member of that staff also received his training in this work in our Aeronautical Laboratories.

The Aeronautical Inspection Department were also indebted to the Laboratory of the North British Rubber Company, Ltd. for the training of some of their scientific staff, and their testing equipment was in many respects also based on the results of this experience.

During the course of the war our output was steadily increased, and at the Armistice we were manufacturing over 35,000 yards of balloon fabric per week, every piece of which was tested in our Aeronautical Laboratories for weight, strength, and hydrogen leakage.

The investigations of the Research Laboratory into the action of light on rubber resulted moreover, amongst other things, in a discovery which without any increase in weight permitted the production of a fabric of vastly enhanced durability, specially suitable for use in the tropical theatre of the war.

Our reason for asking the publication of this communication is only for the purpose of stating that at least one manufacturer was sufficiently well-equipped, not only in the manufacture, but in their scientific staff and laboratories, to carry on without outside help, and it is not intended to detract in any way from the very useful and great assistance which the National Physical Laboratory

gave to Government Departments and others starting out in what was probably new ground to them.—I am, &c.,

L. A. WILLIAMS (Works Manager)
THE NORTH BRITISH RUBBER CO., LTD.

NOTES.

BACTERIA OF THE HEVEA LATEX.—The microbes identified, in experiments by Messrs. Denier and Vernet, as existing in the latex of the Hevea are in number 27 aerobic, or facultatively so, and one anaerobic. These bacteria belong to numerous species. There is the *Coccus* in a cluster, chains or groups of four. The *Cocco-Bacillus* is represented by two species. Bacilli are very numerous, twenty of them were counted. Some have no peculiar characteristic, others are chromogenic and some have a median or terminal spore. These microbes were found irregularly in the various experiments except one which was isolated in all, whatever the medium adopted. It represents the bacteriological constant of this flora. Its biological properties are very extensive. It attacks dambosite which is the sugar of Hevea latex; it is the only microbe with this property. It ferments lactose and saccharose, coagulates milk, liquefies gelatin, but remains without action on coagulated egg albumen. These microbes attack lactose. Saccharose is transformed by 10 bacteria and also by the anaerobic bacillus. The microbes coagulating milk, except one, are very rare. The proteolytic power of these various bacteria was investigated with coagulated egg albumen and gelatin. White of egg is more or less completely digested by 13 bacteria including the anaerobic bacillus, and particularly marked in the case of four. Finally, there are eleven which liquefy gelatin. The first series of experiments demonstrates that the microbial flora, chiefly aerobic, is extremely polymorphous. It is, however, to be noted that one microbe is found regularly in every case, and that it alone acts upon the sugars of the latex of the *Hevea Brasiliensis* which it transforms into acids.—*Caoutchouc and La Gutta-Percha*, September 15, 1920.

MINERAL RESOURCES OF GREAT BRITAIN.—The Ministry of Agriculture and Fisheries desire to give notice of the publication of a second edition of the Seventh Volume of the Special Reports on the Mineral Resources of Great Britain, which have been prepared by the Director of the Geological Survey in response to numerous enquiries that arose through conditions brought about by the late war. Price 5s. net. In the second edition of this Memoir the account of mineral oil, and of the explorations now being made for it in Great Britain, is brought up to date of going to press (June, 1919). In the chapter on Kimmeridge oil the results of analyses made by the Mineral Resources Development Bureau, and further notes on the works in progress in Norfolk have been added. The records of occurrences of cannel coals have been greatly expanded, as a result of recent investigation in all the coalfields of England and Wales. Copies may be obtained, through any bookseller, from the Director-General, Ordnance Survey Office, Southampton.

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MEETINGS FOR THE WEEK.

Monday, December 6.

Royal Institution, 5. (General Meeting).
Royal Society of Arts, 8. "Micro-organisms and some of their Industrial Uses" by A. Chaston Chapman.
Society of Chemical Industry, 8.

Tuesday, December 7.

Society of Chemical Industry. (At Edinburgh).
Royal Society of Arts, 4.30. "The Trade of Australia during and after the War" by A. H. Ashbolt.

Wednesday, December 8.

Royal Society of Arts, 4.30. "Personal Influence of Britons in Russia" by E. A. Brayley Hodggets.

Thursday, December 9.

Royal Society, 4.30.
Optical Society, 7.30.
Institute of Chemistry. (At Liverpool).

Friday, December 10.

Physical Society, 5.

Saturday, December 11.

Biochemical Society. (At Cambridge).

NOTICES.

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H. J. BUTCHART,
Secretary.

ROYAL SOCIETY.

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3054, August 16th, 1918.
3056, September 13th, 1918.
3059, October 25th, 1918.
3062, December 6th, 1918.
3063, December 20th, 1918.
3064, January 3rd, 1919.
3066, January 17th, 1919.
3068, January 31st, 1919.
3069, February 7th, 1919.
3070, February 14th, 1919.
3073, March 21st, 1919.

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3165.

EDITORIAL.

THE following Paper has been received:—

"Is H composed of a Whole-Number Part (a) plus an Auxiliary Part (b) and a Rotating Electron (c)?" By F. H. LORING.

The author presents an argument which has novel features in that it shows how it is within the realm of possibility for the hydrogen atom to be complex and consist of three parts as indicated in the title. Some striking figures are worked out in support of the hypothesis; but the author points out that the matter is speculative, its main merit being simplicity. (Received November 21, 1920).

RELATIVITY: A FEW SELECTIONS FROM RECENT LITERATURE.

By F. H. LORING.

READERS of the CHEMICAL NEWS* may remember an attempt I made in 1915 to elucidate the theory of relativity. This subject has recently become one of general interest, and the extension of the theory to co-ordinate gravitation gives it great prominence. A few passages from current literature should be of interest as, apart from pure science, some of them are very fine from a literary point of view.

H. L. Brose says, in an introductory sketch of the theory published by Blackwell, Oxford, 1919: "Einstein . . . asserts that inertia and gravitation are merely manifestations of the same quality of a body according to circumstances We may now enunciate Einstein's Principle of Equivalence: Any change which an observer perceives in the passage of an event to be due to a gravitational field would be perceived by him exactly in the same way, if the gravitational field were not present and provided that he—the observer—make his system of reference move with the acceleration which was characteristic of the gravitation at his point of observation."

E. Freundlich "The Foundations of Einstein's Theory of Gravitation" (translated by H. L. Brose: published by the Cambridge University Press, 1920) quotes the following beautiful narration by way of illustration: "Let us suppose an explorer to narrate to us his experiences in yonder mysterious ocean. He had succeeded in gaining access to it, and a remarkable sight had greeted his eyes. In the middle of the sea he had observed two floating icebergs, a larger and a smaller one, at a considerable distance from one another. Out of the interior of the larger one, a voice had resounded, issuing the following command in a peremptory tone: 'Ten feet nearer!' The little iceberg had immediately carried out the order, approaching ten feet nearer the larger one. Again, the larger gave out the order: 'Six feet

nearer!' The other had again immediately executed it—and in this manner order after order had echoed out, and the little iceberg had continually been in motion, eager to put every command immediately and implicitly into action."

"We should certainly consign such a report to the realm of fables. But let us not scoff too soon! The ideas, which appear so extraordinary to us in this case, are exactly the same as those which lie at the base of the most complete branch of natural science, and to which the most famous of physicists owes the glory attached to his name."

"For in cosmic space such commands are continually resounding, proceeding from each of the heavenly bodies; from the sun, planets, moons, and comets. Every single body in space harkens to the orders which the other bodies give it, always striving to carry them out punctiliously. Our earth would dash through space in a straight line, if she were not controlled and guided by the voice of command, issuing from moment to moment, from the sun, in which the instructions of the remaining cosmic bodies are less audibly mingled."

"These commands are certainly given just as *silently* as they are obeyed; and Newton has dominated this play of interchange between commanding and obeying by another name. He talks quite briefly of a mutual attractive force, which exists between cosmic bodies. But the fact remains the same. For the mutual influence consists in one body dealing out orders, and the other obeying them."

A. S. Eddington in "Space Time and Gravitation" (Cambridge University Press, 1920) referring to the work at Principe in photographing the eclipse of the sun in order to test Einstein's theory, says: "The observers had rather more than a month on the island to make their preparations. On the day of the eclipse the weather was unfavourable. When totality began the dark disc of the moon surrounded by the corona was visible through cloud, much as the moon often appears through cloud on a night when no stars can be seen. There was nothing for it but to carry out the arranged programme and hope for the best. One observer was kept occupied changing the plates in rapid succession, whilst the other gave the exposures the required length with a screen held in front of the object-glass to avoid shaking the telescope in any way."

"For in and out, above, about, below

'Tis nothing but a Magic *shadow-show*

Played in a Box whose candle is the Sun

Round which we Phantom Figures come and go."

"Our shadow-box takes up all our attention. There is a marvellous spectacle above, and, as the photographs afterwards revealed, a wonderful prominence-flame is poised a hundred thousand miles above the surface of the sun. We have no time to snatch a glance at it. We are conscious only of the weird half-light of the landscape and the hush of nature, broken by the calls of the observers, and beat of the metronome ticking out the 302 seconds of totality."

Passing over several pages of most interesting reading matter I will now quote some statements of the results.

"It will be remembered that Einstein's theory predicts a deflection of $r''74$ at the edge of

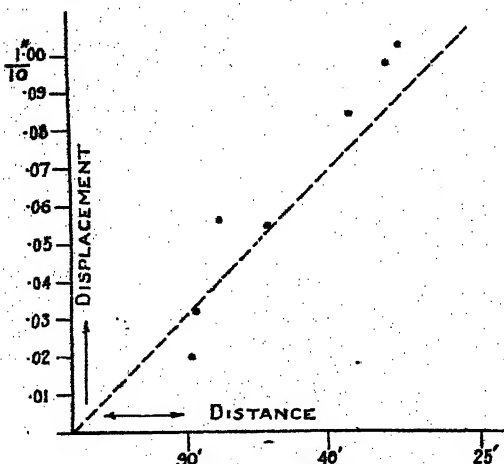
*CHEMICAL NEWS, cxli, 226, 236, 248, 260, 306 correction, and 322.

the sun, the amount falling off inversely as the distance from the sun's centre. The simple Newtonian deflection is half this $0''.87$. The final results (reduced to the edge of the sun) obtained at Sobral and Principe with their 'probable accidental errors' were

$$\begin{aligned} \text{Sobral } 1''.98 \pm 0''.12 \\ \text{Principe } 1''.61 \pm 0''.30 \end{aligned}$$

It is usual to allow a margin of safety of about twice the probable error on either side of the mean. The evidence of the Principe plates is thus just about sufficient to rule out the possibility of the 'half-deflection,' and the Sobral plates exclude it with practical certainty. . . . The theoretical deflection should vary inversely as the distance from the sun's centre; hence, if we plot the mean radial displacement found for each star separately against the inverse distance, the points should lie on a straight line. This is shown in Fig. I, where the broken line shows the theoretical prediction of Einstein, the deviations being within the accidental errors of the determinations. A line of half the slope representing the half deflection would clearly be inadmissible." (The figures here given are substantially the same as the originals).

FIG. I.

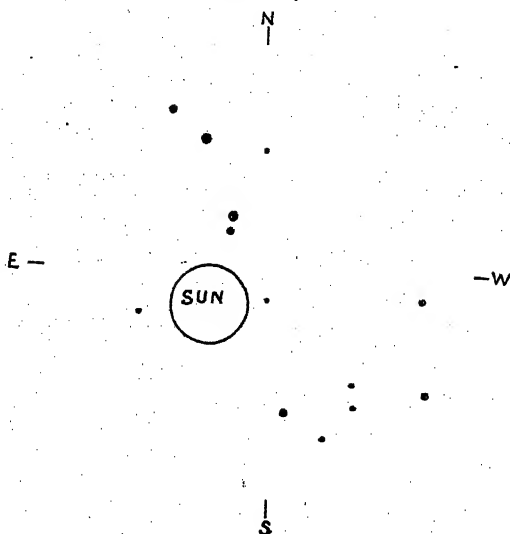


"A diagram showing the relative positions of the stars is given in Fig. II."

A. Einstein says in "Relativity: The Special and General Theory" (translated by R. W. Lawson: published by Methuen & Co., London, 1920): "We are indebted to the Royal Society and to the Royal Astronomical Society for the investigation of this important deduction. Undaunted by the war and the difficulties of both a material and a physiological nature aroused by the war, these societies equipped two expeditions—to Sobral (Brazil), and to the island of Principe (West Africa)—and sent several of Britain's most celebrated astronomers (Eddington, Cottingham, Crommelin, Davidson), in order to obtain photographs of the solar eclipse of May 29, 1919. The relative discrepancies to be expected between the stellar photographs obtained during the eclipse and the comparison photographs amounted to a few hundredths of a millimetre only. Thus great accuracy was necessary in making the adjustments

required for the taking of the photographs, and in their subsequent measurement. The results of the measurements confirmed the theory in a thoroughly satisfactory manner."

FIG. II.



The works referred to should, of course, be read by all interested in the general subject of relativity and gravitation. In Einstein's book, a list of the English writings on this subject is appended; 16 references are given.

Note.—In my article, p. 322, the value 0.454 should read 0.451 and the value 0.451 should read 0.454.

THE ORIGIN OF PRIMARY ORE DEPOSITS.*

By J. MORROW CAMPBELL.

Introduction.

THE object of this paper is to review briefly the present theories of the origin of Primary Ore Deposits, to indicate some of the directions wherein accepted theories fail to account for observed phenomena, and to put forward a theory which, it is believed, will help not only to explain the segregation, transport and deposition of ores, but also to place the larger question of magmatic segregation on a simpler and more rational basis.

The problem is one of fundamental importance to both mining men and geologists.

The field to be covered is so wide that it is impossible within the limits of space available to deal more than superficially with the many points that demand consideration.

The Outer Crust of the Earth.

Ore minerals are obviously derived from the outer crust of the earth, and their concentration into deposits of commercial value is effected by natural processes.

The statement that ores are derived from rock magmas has become a commonplace, for it is

*From *Bulletin of the Institution of Mining and Metallurgy*, October, 1920.

generally admitted that the crust of the earth, to depths much greater than are likely to be accessible to us, passed through a molten phase, and was practically rock magma previous to solidification. In order to deal adequately with the problem, it is essential to consider it from as early a stage as possible.

Two theories of the origin of the earth find acceptance:—(1) The Gas Nebular Theory and (2) The Planetesimal Hypothesis. For present purposes it is probably immaterial which we accept.

According to (1) it is quite obvious that the crust must have passed through the liquid between the original gaseous and the present solid state. Daly ("Igneous Rocks and their Origin," pp. 155-160) proves conclusively that the conditions postulated by the Planetesimal Hypothesis necessarily resulted in a molten exterior layer, and it as well to state the conclusions he accepts as being involved by both theories; "(a) A former molten stage for the earth's exterior crust; (b) The density stratification of the planet; (c) A fairly uniform composition for the surface shell; (d) General magmatic temperatures, not more than a few miles below the surface throughout geological time."

The surface was molten for a considerable period, and must have consisted of silicates with ore minerals in solution. Material below this increases in density, and we conclude it contains more of the heavy metals. Some regard it as approximating to metallic meteorites in composition. It is fairly safe to assume that material below the silicate crust did not contain either oxygen or the elements of water, and does not at present.

While the silicate layer was molten, the atmosphere must have contained at first practically all the water in existence, also much more oxygen and carbon dioxide than it does at present. Absorption of oxygen took place actively at the surface, but the process was slow relatively to the volume of liquid, for, if convection currents existed, they could not have been rapid.

It has been the custom of geologists to assume the existence of two types of primary magma—the granitic above and the basaltic below. Others believe that the initial crust of the earth was basaltic, and that a granitic magma developed beneath it.

The truth is probably reached by assuming the existence of only one primæval magma, of intermediate composition—dioritic or andesitic—which on differentiation yielded both the typical granitic and basaltic magmas.

We must attempt to picture how the primary crust developed. Solidification commenced at the surface by radiation of heat as ice does on water, but the result differed in that the solid was heavier than the liquid; therefore, upon being broken up by tidal and storm movements, it sank and was re-melted. This cycle of crust formation, foundering and re-fusion proceeded until the temperature of the silicate sea to a depth of probably several miles was very considerably lowered. At this stage the temperature gradient in the exterior layer came to be of an order of magnitude approximating to that which obtains at present. Loss of heat through solid silicates by conduction is so extremely slow that the present low temperature gradient in the crust would be impossible

unless there were a process such as we assume by which the silicate layer while still liquid was reduced to a fairly uniform temperature throughout.

Permanence in the crust could not have been attained until the viscosity of the liquid, consequent on cooling, had increased to such a degree as to render foundering impossible.

The silicates whilst molten absorbed water from the atmosphere, but at what temperature this commenced it is impossible to say. This water is believed to have entered into combination with silica and silicates as hydroxyl, and not to have been merely dissolved as water. The difference may seem of small importance, but is probably fundamental. As the crust froze and foundered, the elements of water were carried downward and dispersed through the molten material. It seems certain that the permanent crust formed long before the whole of this primæval magma was saturated with the elements of water. The result of this absorption of water was differentiation of the silicates (which we have assumed to be of intermediate type) into a granitic surface layer, which solidified first, and below it a still liquid basaltic magma. The reason why differentiation took place will be explained below.

The initial crust was therefore granitic in composition, but it did not solidify peaceably. Cooling caused contraction, and this with other forces produced contortion and fissuring. Vast volumes of basic lava poured out and solidified, bringing heavy metals to the surface, and introducing complexity into the crust. It was during this stage, which lasted for a prolonged period, that the earth assumed its general tetrahedral form, and that the isostatic balance was adjusted.

There is every reason to believe that the two typical magmas while yet molten were immiscible.

On the strength of laboratory experiments some authorities assert all rock melts to be immiscible. This is quite true for atmospheric pressures *in the absence of water*. The mere fusion of granite and basalt demonstrating their miscibility at any temperature or pressure has no bearing on the question unless the experiment is conducted with the elements of water present in quantity such as occurs in nature.

We have evidence indicating that granitic magmas on solidification give off an aqueous mother-liquor. The primary crust was largely granitic, so we have to assume that it gave off a similar liquid. Such acid liquors invariably carry the bulk of the ore minerals originally present in the granite magma, so we must assume that large quantities of ores were ejected at the surface of the primary crust. These would be mostly tin, tungsten, gold, copper, zinc and lead.

Probably none of these primitive ore deposits have survived; they must have been denuded—dispersed in sediments and in aqueous solution. The vast quantity of gold and other metals in solution in the sea is probably derived from this source. Some of these primæval ores that were enclosed in sediments were leached out later and deposited in veins in other sediments at higher levels. This is a possible explanation of the origin of ore deposits which appear to have no igneous rock in their vicinity from which they could have emanated. Other ore-bearing sediments have doubtless been absorbed in intruded magmas from which on differentiation they

developed a second time in veins. Daly adduces evidence from actual observation so strong that we must attach great importance to magmatic stoping and, as such stoping necessarily involved the absorption of much ore, it may account in at least some measure for the seemingly erratic mode of occurrence of primary ores.

We assume that the first rock to solidify was granite, but this was intruded by a large quantity of more basic material. Below this the basaltic magma remained molten for a considerable time. It is generally believed that this also assumed the solid state at the commencement of geological time. Some geologists believe that pools have remained liquid even till the present time. This is a debatable point and, as it has no important bearing upon the subject under consideration, it may remain open.

Primary Ores.

Primary ores may be defined as those which are derived directly from rock magmas or magmatic liquids and have not undergone any essential change since their segregation or deposition.

It is probable that some ore deposits formed by segregation of dispersed primeval ores and deposited in veins at a higher level, and which are thus only indirectly derived from magmas, should also be regarded as primary. The distinction between these and true primary ores might be difficult to establish.

As the segregation of ores or ore-bearing liquid from rock magmas is part of the process of magmatic differentiation it is necessary for us to follow that process and understand it as far as possible.

The Formation and Differentiation of Rock Magmas.

(a) *General.*—Rock magmas are generally regarded as forming from solid material owing to an increment of heat. This heat is supposed by some geologists to have a mechanical origin. Others regard it as being generated by the oxidation of elements. To both theories there are serious objections. On one, and only one, point is there agreement—all rock magmas contain water. This is probably untrue. Such magmas as undergo differentiation certainly contain the elements of water and on cooling give off water, but this does not prove that as magmas they contain water *qua* water. As regards the origin of this "water" there is more disagreement. It seems to be the general belief that water is an original constituent of all magmas; others believe it may have its origin in hydrogen, occluded in the barysphere, which has taken up oxygen at the expense of oxides; still others regard it as of meteoric origin.

First, we must enquire as to the source of the heat which induces the molten condition in already solidified crustal material. It is generally conceded that the temperature in rock magmas is over 1000° C., which is far above the critical point of water. The maximum temperature recorded in molten lava is certainly below the melting point of silica. Silicates are said to have been sublimed in volcanic vents and, if this be true, a temperature even above the melting point of quartz may exist in rock magmas at great depth, for it is unreasonable to suppose that on its way upward it does not lose heat. Though there is no reliable record of temperatures exceeding 1500° C. in lava

pools, we must not assume that they are not of a much higher order at the source. It is only during quiescent periods that records can be secured, and at such times molten material is either welling up very slowly or temporarily stationary. We may reasonably suspect that during periods of great activity lava temperatures even at the vents may be much higher than any yet recorded, and that at their point of origin rock magmas may be far above their melting points. If such be the case it is improbable that the fusion of magmas is due to mechanical causes.

That heat is produced by the oxidation of elements is unlikely, as it is difficult to imagine whence oxygen can be derived.

That pools of molten rock at a temperature much above its melting point can exist in the crust for prolonged periods is impossible.

It appears that all lavas give off gases among which are water or the elements of water, also that all rock magmas as the result of differentiation give off an aqueous liquid.

The material from which rock magmas develop is of igneous origin, and is itself the result of differentiation of primeval molten crustal silicates that solidified or segregated under conditions which render it unlikely that it contained large quantities of the elements of water. It savours of the ridiculous to assert that such material could retain, either in solution or combination, in its solid products of differentiation an amount of the elements of water much greater than it can retain when the same material after re-fusion undergoes differentiation at a later period. We are practically forced to admit that the material forming rock magmas receives an increment of water between the date of formation of the earth's crust and the time when it undergoes differentiation as a batholith or is ejected as lava.

The writer regards magmatic differentiation as being brought about mainly if not entirely by means of water, and believes that to the absorption of water of meteoric origin is due the liquefaction of rock that had solidified in its practical absence during the formation of the crust.

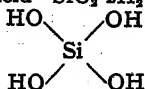
(b) *Silica, Water, and Silicic Acid.*—Let us now study the evidence that nature and the laboratory furnish regarding silica and water.

If they are heated together at atmospheric pressure no action takes place. If amorphous silica and water are placed in a sealed tube and heated to 200° C., a liquid results which deposits silica in crystalline form as quartz. We must try to ascertain whether this is a case of simple solution or of chemical combination. Since silica enters in the amorphous state and comes out as crystals, it is evident that molecular re-arrangement has taken place—this suggests combination. Since water at 100° C. does not dissolve silica appreciably, it is unlikely that it could do so *freely* at 200°. We have very good reason to suspect that chemical combination takes place at the latter temperature.

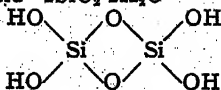
Silicates are comparatively simple compounds, since the structural formulæ indicate that silicon in a silicate molecule cannot unite directly to silicon, but indirectly through one or two oxygen atoms. It is fortunate that in this respect it differs from carbon, otherwise the silicon compounds might have been as numerous as those of carbon.

Following the silicate types, the simplest of the series of silicic acids are:—

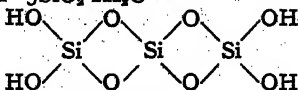
Ortho-silicic acid = $\text{SiO}_2 \cdot 2\text{H}_2\text{O} =$



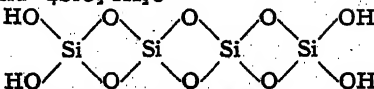
Meta-silicic acid = $2\text{SiO}_2 \cdot 2\text{H}_2\text{O} =$



Tri-silicic acid = $3\text{SiO}_2 \cdot 2\text{H}_2\text{O} =$



Tetra-silicic acid = $4\text{SiO}_2 \cdot 2\text{H}_2\text{O} =$



and so on to, perhaps, much longer-chain molecules.

It will be noticed that in this series each member differs from the next by SiO_2 .

It seems probable that silica and water combine to form orthosilicic acid, and that this can take up silica when conditions are favourable, forming the longer-chain molecules. To what length they extend we cannot say, but we may infer that the greater the pressure the longer they may be.

Altered conditions such as affect a cooling magma or mother-liquor cause the long-chain silicic acid molecules to give off silica. This is deposited as quartz till about 180°C . is reached. At lower temperatures crypto-crystalline silica develops, and, still later, non-crystalline varieties such as opal and sinter. The latter are probably derived from ortho-silicic acid, but, even at the surface, this dissociation is not complete, for the amorphous varieties of silica always hold some hydroxyl in combination.

When an acid magma crystallises under pressure we have a highly acid mother-liquor given off. We come to this conclusion on the evidence of pegmatite and quartz veins, one or both of which are invariably found in and above granite batholiths. These veins were not filled by quartz or pegmatite in a state of simple fusion and there is no doubt that the elements of water were present in the liquid from which they were derived. It is generally conceded that the lowest temperature at which this liquor could have left the batholith was 500°C . It cannot be denied that the two most abundant products of this liquor are quartz and water, therefore we may regard silicon and the elements of water as the two essential constituents when it left the granite. Since its temperature is about 150°C . above the critical point of water the latter, if present as water, must be as dissolved gas. The other essential constituent is silicon which, if present as silica, should be a solid more than 1000° below its melting point. That these two substances could, by simple mixture, produce a liquid is absurd. This is strong presumptive evidence that combination takes place and that the elements of water are present in it as hydroxyl in combination with silicon.

Experiment has proved that at high temperatures and pressures water and silica form a liquid. We must assume that silicic acid is formed, that it is capable of dissolving silica freely and that it is miscible with water.

The so-called hydrated silica deposited by thermal waters represents only a small quantity of the silicic acid that was present at higher temperature and pressure.

Silicic acid is also present in water other than that of magmatic origin, for we find fossil wood in which hydrated silica replaces cellulose.

The hard parts of infusoria and other forms of marine organisms consist essentially of opaline silica.

Certain plants also secrete hydrated silica.

It is argued that the only hypothesis consistent with known chemical and physical laws capable of explaining the phenomena recounted above is that at elevated temperatures and pressures as well as in vital processes silica and water combine to form silicic acid.

The range of temperature through which this reaction is possible is not known.

It has been asserted that water present in rock magmas acts as an acid even replacing silica in silicates. There does not appear to be much evidence in support of this theory. "Water" in magmas appears to be present as hydroxyl in combination with silica. No magmatic minerals are hydrated in the true sense of the term; many contain hydroxyl which acts as a basic radicle, the hydrogen of which takes the place usually of alkali metals, either wholly or in part.

Instead of replacing silica, water, when absorbed by magmas, combines with it, decomposing silicates with the liberation of those bases whose affinity for silica is weakest.

(c) *Rocks resulting from Magmatic Differentiation.*—Rocks resulting from the differentiation of primeval crustal magma or of subsequent rock magmas whether produced by the refusion either of various fractions of the former or of sediments are termed igneous rocks. As the name indicates, they appear to be the result of the solidification of fused materials.

They vary in composition from nearly pure quartz at one extreme to nearly pure metallic oxides and even metals at the other. Between these extremes we have a great variety of rocks of an intermediate composition. We believe all these to have been derived from one original liquid silicate mixture.

All silicates appear to be mutually soluble at high temperatures in the absence of water, therefore, we should admit that the primeval silicate magma was practically uniform in composition throughout, and, under the conditions at the time, approaching a state of stable equilibrium. Changing conditions, consequent upon cooling, upset this equilibrium, and the tendency ever since has been towards heterogeneity. It has been a period of transition from the fluid to the solid state, the latter being the only one in which absolutely stable equilibrium is attainable.

Magmatic differentiation is the ponderous name given to the process whereby rocks in almost infinite variety have been evolved from a molten mass of uniform composition.

To assume anything short of homogeneity to begin with, must be an error.

The agent which produced the first great split in the primæval silicates is almost certainly the one whose continued action has resulted in the present seeming confusion. We may hope that identification of this agent will do much to establish order where chaos now reigns.

(d) *The Magmatic Differentiation Process.*—It is probable that the primæval crustal magma was between syenite and diorite in composition, with about 60 per cent of combined silica and without water.

This magma underwent differentiation as a whole, therefore we cannot expect to find anything exactly similar in composition at the present time.

The first step towards differentiation was the absorption of water from the atmosphere, which combined as hydroxyl liberating ferrous oxide principally. This oxidised largely to Fe_2O_3 . As more water was absorbed the longer-chain silicate molecules lost silica which with hydroxyl gave rise to free silicic acid. This in turn formed a solution with potash aluminosilicate which appears to be immiscible with or very sparingly soluble in a rock melt containing ferro-magnesian silicates and basic feldspars. This series of reactions proceeded during the cooling period previous to the development of the permanent crust. Masses of foundering crust kept the whole in a state of agitation, and supplied oxygen and water from the surface. As time advanced these masses increased in size and descended to greater and greater depths in the cooling silicate sea before being absorbed. In this way the leaching of potash compounds proceeded to great depths, density stratification was prevented, and a gentle temperature gradient established. The crust became permanent long before the capacity of the fused silicates for the absorption of water and oxygen was satisfied; then general absorption was prevented, and the molten mass, no longer in violent agitation, underwent segregation into an acidic portion above and a basic portion below. The upper layer developed as granite and the lower—practically a true rock melt of basaltic composition—probably remained molten, in part at least, for a considerable time.

The top of the crust was probably not truly granitic in composition but considerably more basic, since it was only after its formation that segregation upward of the acidic sub-magma could have taken place.

The first component of ordinary granite to assume the solid state is biotite; this is followed by feldspar, the two forming a mass of interlacing crystals. The interspaces are filled by quartz deposited from silicic acid solution, while the mother-liquor with the ore minerals in solution is forced out usually through fissures.

The first split in the primæval magma thus yielded granite as a solid roof with a basaltic layer below. As the process described must have acted practically uniformly in the whole outer crust, we should have at a depth of several miles a layer of basaltic material very uniform in composition everywhere round the globe. Daly draws attention to this uniformity as actually existing, and even assumes the basaltic type to have been the primary earth magma.

As we are primarily concerned at present with ore deposits, full consideration of magmatic segregation in general must be deferred.

The writer is in agreement with Daly as to the great importance of syntaxis, and admits that much of the later granite may be the result of magmatic stoping by basaltic magmas. In this connection it may be remarked that very little importance is attachable to the belief or disbelief in the existence of molten basaltic pools. The present contention is that they cannot undergo magmatic differentiation unless or until water reaches them; if they could it seems somewhat remarkable that their ability to do so should have remained in abeyance for millions of years.

(To be continued.)

GAS MANUFACTURE AND CHEMICAL INDUSTRY.

CHEMICAL engineering problems, in relation to gas manufacture, were dealt with by the new President of the Midland Junior Gas Association, Mr. W. J. Pickering, Gas Chemist (Midland Section Society of Chemical Industry) and Superintendent Coal Test Works, Birmingham Gas Department, in his presidential address recently given before a full attendance of members. He pointed out that chemical plant on gas works tended, and rightly so, to increase in extent, and at many works junior chemists had definite duties on such plants. He knew of some medium-sized works where the ammonia washing and scrubbing plant was directly under the control of a junior, and good results as regarded efficiency of washers and strength of liquor made for sale, were achieved. Whatever the plant might be, a measure of responsibility in this way should be welcomed. The field for the engineering chemist on modern works was of increasing importance, and several problems which had a bearing on this particular question could be mentioned. Oxide purification was an instance where little change in apparatus and methods of working had taken place for many years. The purifier box had remained almost as it existed to-day for more than 50 years, and the question of the use of oxide of iron for H_2S removal was one which was not even yet fully understood in all details. A fair amount of careful and fairly successful research which was carried out prior to the war, on methods of liquid purification of gas and work on those lines would, no doubt, be proceeded with as opportunity offered. Valuable ground space would be saved by a reduction in the number of purifier boxes, and cost of purification would be reduced as regarded labour required for box changing. Naphthalene troubles had afforded considerable scope for the gas works chemist, as careful investigation was necessary before any particular method of cure or prevention was adopted. Regular testing by way of supervision was also essential to secure proper working efficiency of whatever plant was installed. The problem had cropped up in slightly different form during recent years owing to the "stripping" of gas for extraction of crude benzol, which had thereby reduced the "hydrocarbon content" of the gas, and also by reason of the fact that gas leaving the works had been, generally speaking, at a higher temperature owing to the larger volume of gas made per unit of carbonising plant. It would seem that the best method ultimately of dealing with the naphthalene problem would be by way of removal of the naphthalene at as early a stage as possible on the

gas stream. Dr. Carpenter's method of "shock-cooling" the gas in specially-designed water-cooled condensers and at the same time washing the gas with thin tar was modern practice in this respect. The naphthalene question was aggravated by deposits of the crystalline compounds in the mains on many large works, and until those were removed, methods of washing or spraying the gas with "cold" solvents would need to be continued in order to prevent the gas picking up and carrying forward naphthalene from those deposits on to the district. Recording instruments for indicating both pressure and quality of gas were an important feature on most large works, and the care of those usually fell to the chemist. Properly looked after so that their readings might be relied upon, those instruments were of undoubted help to the engineer, but regular supervision and checking was very necessary. The installation of instruments recording calorific value and specific gravity, on works streams of coal gas and water gas would give timely indication of fluctuations in gas quality; and occurrences in the retort house and elsewhere which might otherwise not be detected until more time had elapsed, could be quickly dealt with. It was very probable that, in the near future, instruments of that nature would be placed out at certain points in the distribution area, under the Gas Regulation Act, and very useful data should then be forthcoming.

THE COAL FIRE.

WITH the object of diminishing the smoke nuisance in Manchester, a committee of the corporation, in a spirit of far-sighted and eminently practical enquiry which might well commend itself to other municipalities, appointed some few years ago an "air pollution advisory board" to enquire into the efficiency of domestic fire-places. The executive was composed of factory managers, local men of science, city councillors, and others. Under their auspices and that of the Fuel Research Board, Dr. Margaret Fishenden, late Beyer Fellow of the University of Manchester, was appointed to undertake the research which has been in part financed by the Department of Scientific and Industrial Research. The results are embodied in a very full report on "The Coal Fire," (a Research by M. W. Fishenden, D.Sc.) which has been published for the Fuel Research Board by H.M. Stationery Office. In view of the facts that of the 190 million tons of coal which are consumed in the United Kingdom annually, rather more than 40 millions, or about one-fifth, is burnt on the domestic hearth (*Jour. Royal Soc. Arts*, 1917, p. 136), and that the domestic chimney is responsible for much the largest proportion of soot of a peculiarly tarry and adhesive nature, any improvement which would lead either to the more economic use of coal by increasing its heating efficiency, or to diminished emission of smoke, would be of untold advantage to the community. The report is therefore of peculiar value, as up to the present no very trustworthy information on the subject has been forthcoming.

The method employed has been substantially that used in the Leeds tests in the investigation of gas fires ("Reports of the Gas Heating Research Committee of the Leeds University," 1919-1920).

The radiant efficiency was estimated by the percentage of B.Th.U. in the fuel used in radiation in the following way:—

An imaginary hemisphere, of which the radiating surface is the centre, is mapped into areas by lines of latitude and longitude 20° apart, so that in all there are 81 areas, which naturally vary in dimensions, being largest at the equator and decreasing towards the poles. The amount of radiation falling on the central area is estimated by means of a radiometer; the total amount calculated in B.Th.U. being determined from the lighting of the fire until its extinction. The radiation falling on the other surfaces of the hemisphere was determined by comparing the readings of a thermopile placed in the centre of each area and adjusted on a pivoted metal "line of latitude." It was found unnecessary to go through the whole series in each experiment, as "the distribution factor," as it is termed, varies very little for the same grate. This factor is the sum of the relative values of the thermopile readings corrected for the different areas, taking the central area as unity, and was found to be 32.5 in the first grate investigated. The "radiant efficiency" for this grate is given by the expression

$$\frac{R \times 32.5}{C} \times 100$$

in which R is the total heat absorbed by the radiometer from start to finish expressed in B.Th.U., and C is the calorific value of the fuel in B.Th.U. Thus, the expression represents the percentage of B.Th.U. utilised in radiation.

A variety of grates was examined in this way with varying rate of air-current regulated by a damper, and with coal of different qualities and in different states of aggregation, patent fuel preparations, anthracite, coke carbonised at high and low temperatures, and briquettes.

In addition to these determinations, measurements were made of heat absorbed by the air passing up the chimney from different kinds of fuel, and of the effect of restricting the draught. The heating of the air of the room under different conditions of draught was also estimated. Without discussing these observations in detail, we may give briefly the author's summary.

There was little alteration in the radiant efficiency of coal; it varied from 19.5 to 24 per cent, burnt in different types of grate, which showed no advantage in favour of the modern grate (crushed coal—slack—lowered the efficiency from 24 to 20 per cent), nor was the radiant efficiency affected by the rate of combustion. With other kinds of fuel, however, a notable increase was observed, anthracite giving 27, coke 28.5, the low-temperature coke 34 and 31, as compared with coal at 24. Briquettes, on the other hand, gave 19 per cent efficiency. Although the total radiation showed a comparatively small range of variation, the design of the grate affected its distribution, a vertical radiating surface having an advantage for the occupant over a horizontal one. Subject to considerable variation, the average value of the air flow was 19,000 cubic feet per hour, the temperature of the flue at the ceiling level being 105°F. , as compared with 53°F. for that of the entrant air.

The author estimates that in the case of a coal fire burning with a full draught giving 22 per cent radiation, about 52 per cent of the heat of

combustion is lost in passing up the flue, so that the heat absorbed by the brickwork would not amount to more than 20 per cent. For an outer flue this is mainly wasted. With restricted draught, on the other hand, the flue loss could be reduced to about 13 per cent. The difference of 39 per cent is ascribed by the author to heat dissipated by conduction through the flue walls owing to the lowered rate of air flow. The importance of building flues on inner walls becomes obvious, as well as the advantage of restricting the draught which thereby diminishes the flow of cold air through the room and lowers the rate of combustion. The author also draws attention to the radical importance of a grate being as little recessed as possible, so that no obstacle should screen off the radiation. In conclusion, Dr. Fishenden refers to the relative cost of coal, gas, and electricity. Taking the heating efficiency of coal (including heating of air, walls, and brickwork) as at least 30 per cent, the modern gas fire at 60 per cent, and the electric heater at 100 per cent, and assuming coal to cost 45s. per ton, gas 4s. 6d. per 1000 cubic feet, and electric power at 1d. per unit, the cost of a coal fire for continuous heating is only about one-third that of a good gas fire, and one-fifth that of an electric fire of equal heating capacity.—*Journal of the Society of Chemical Industry*, October 15, 1920.

DYES AND THE TEXTILE INDUSTRY.

SPEAKING at the adjourned discussion of this subject at the House of Commons Commercial Committee, Mr. W. J. U. WOOLCOCK, C.B.E., M.P., said:—

"In intervening in this most interesting discussion on the relation of the manufacture of dyes in this country to the textile industry, there are two methods of treating the subject which I can follow. It would be possible to take the interesting paper to which we listened last Wednesday and traverse each statement one by one, but I think this would be rather unfair to Mr. Briggs, who frankly stated that he had no first-hand information on this subject but was merely repeating what he had gathered from various sources—some of which were reliable. I therefore discard this method and if you will allow me I will endeavour to compress into as short a time as possible an outline of the position as it is to-day with the material factors which have led to this position.

The outstanding feature which is bound to strike any careful enquirer who attempts to review the history of the dye industry in this country is that the industry has never had a fair chance of development. To undertake such a task at any time would be difficult, but to attempt it in the middle of a war when the production of explosives, poison gases, and other essential materials had turned dye works into chemical arsenals was an almost superhuman task. Moreover, the industry was handicapped from the commencement by the fact that the extent of the problem was never fully realised. It was thought to be a question of making dyes; it is infinitely more than that. Long before it became a matter of producing the colour, intermediates have to be made, and further back still, adequate supplies of raw

materials for the making of the intermediates have to be assured, and again, markets have to be found for the by-products. The problem was, in fact, comparable with that of producing munitions during the war, but whereas in that case every firm in the country which could produce anything to help was given its quota of work to be done, in the dye problem all the eggs were placed in one nest and we must not be surprised if the resulting brood is neither so numerous nor so fine as was hoped.

It is an astounding fact that there was no attempt made at any co-operative effort in which manufacturers of heavy chemicals, of fine chemicals, of tar products, and of explosives were induced to play their part. All this was impressed on the Government by the Association of British Chemical Manufacturers more than two years ago, but the result has not been proportional to the effort then made, and if the House of Commons does not insist on the problem being dealt with immediately, the country may find itself in a perilous condition. The language I have used may seem strong, but I use it deliberately. *Why may the position become perilous?* If we fail to establish a dye industry in this country, why are we any worse off than if we fail to establish, or lose any other already established industry? The answer is that the national safety of the country is to-day dependent on its chemical industry, and will become more and more so as chemical science is increasingly used in modern warfare, and in every-day life, particularly in relation to agriculture. The loss of 2 million pounds' worth of trade in dyes per annum is not in itself a sufficient reason for special treatment of the industry, it is the loss which follows from this which is so serious. If we lose or fail to develop our dye industry we lose the very plant and machinery on which we shall have to depend if another war is thrust upon us. We shall also have failed to train the particular kind of chemist on whose brains we shall have to rely in the next emergency.

On the top of all this there is the danger of the ultimate destruction of our great textile industry. I trust you will allow me to develop this point because I fear that in too many minds the general impression has been made that all textile makers want free imports of German dyes, and all dye-makers want the total prohibition of imports of German dyes. This is a generalisation which is dangerous. There are textile makers who, now the war is over, are anxious for the free importation of German dyes. Their desires are not based on any particular economic doctrine, and their point of view is well worth considering. It is usually expressed in this way: 'The value of our textile industry is one hundred times as great as that of the dye industry. To hinder in any way the free import of German dyestuffs is to kill the textile industry. It is foolish to throw away 200 millions of textile business for the sake of two millions of dye business.' This argument, left at that point, is sufficient for those whose outlook is limited or the verbiage of whose political decalog is of more importance than the realities of life. Why should we trouble to establish a dye industry in this country when Germany can sell us all the dyes the textile industry wants? If you suggest in reply that if there were no British dye industry perhaps Germany might cease to supply

them with dyes or might supply them, at a price which would make it impossible for them to compete in the world's markets, you are told with an air of finality that we had no dye industry before the war and Germany never withheld or charged high prices for her dyes. Thus we underrate the intelligence of our competitors and wilfully shut our eyes to the psychology of the German industrialists.

Anyone who believes that Germany kept our textile industry going before the war, or will continue to do so after the war, for any other reason than that she is not yet ready to do otherwise, entirely fails to appreciate the German commercial brain. We never have sufficiently understood what I call the Duisberg mind, nor his wonderful creation the *Interessen Gemeinschaft*. Hence, I say that the position might become perilous for the nation, and especially dangerous to the textile industry, if we do not establish the manufacture of dyes in this country.

Remedies. If I carry you with me in my contention that it is essential for the safety of the nation that we should have a dye industry in this country, and that, let it be noted, in the interest of textile manufacturers as much as of everybody else, then let us consider the methods whereby this can be brought about. Two things are essential: (1) that the Government should take a wider view of their responsibilities and encourage the co-operation of all who can assist. I will not enlarge on this point to-night. (2) That the Government should at once (next year will be too late) introduce a Bill granting some assistance to the industry for a few years. Now the question is, "What form shall this assistance take?" This problem has engaged the attention of those best fitted to solve it for many months. My personal view is that every possible form of protection is bad, but that some assistance is necessary; and I therefore approach the problem with the idea of finding the least objectionable form in which assistance can be given. There are five different ways in which it might be done; let us examine them for a moment.

1. **Tariff.** This has only to be stated to be rejected at once. The absurdity of the amount necessary to allow for the difference in the rate of exchange alone kills this method with ridicule.

2. **Subsidy.** Most Government subsidies have been withdrawn, and the inveterate effect of subsidies is too well known to admit of their being granted on a large scale in the case of the dye industry.

3. **State Purchase and Sale Bureau.** The essence of this method is that it should be made compulsory that both the purchase and sale of imported dyes should be made through a Central Bureau in which the Government should be interested, together with men of commercial and technical knowledge. This method overcomes some of the difficulties inherent in other proposals, but introduces additional difficulties of its own. It would necessitate the setting up of a special and rather expensive organisation. This is to be deplored, but what really kills the idea is that we have not at the moment the experts, who would have to be independent of any particular firm, and who would be required to staff the Bureau.

4. **Licensing plus a Tariff Fee.** The idea here is that an importer should be able to obtain a

licence as of right (thereby eliminating the uncertainty of the ordinary system of licensing) but that he should be charged a subscription fee, which would vary with each article, and which would be based on the difference in price between the foreign-made article and that of British manufacture. The chief attraction of this method is the removal of the uncertainty whether a license will be granted or not. In effect it is an easily varied tariff under another name. It has all the disadvantages of an ordinary tariff, and one more. I cannot imagine the House of Commons entrusting any body of persons other than itself with the right to fix and vary a tariff.

5. **Licensing.** Mr. Briggs has quoted Lord Emmott as saying that he knew from his experience in the War Trade Department that it was impossible to conduct a licensing system fairly. I do not know whether Lord Emmott is correctly reported, but if so it is rather a sweeping statement to make. One might say, for example, that a licensing system had not been fairly conducted, but to say that it is impossible to conduct it fairly is to make a statement which I for one with the greatest respect beg leave to doubt. As recently carried out it sometimes results in delays, and is apt to be irritating to the importer and user, but it does not entail some of the disadvantages which are common to other forms of protection. It is, in fact, the least objectionable of all the forms of assistance which can be given to the dye industry, and if re-introduced with one essential modification, would, I think, meet the case. Let us bear clearly in mind what is the object we have in view. It is not to prohibit the import of foreign dyes merely because they are foreign, or to enable British manufacturers to carry on their business without fear of competition. It is to encourage them to spend money on plant and on research work, and then to assist them to so co-operate that in a short time they can stand alone and fight their own battles. I therefore suggest that you cannot do better than adopt a system of prohibition except under licence, with this important modification, that it is understood that licences, for any particular dye which is needed should be freely granted as of right, unless and until the British manufacturer has shown cause why the particular dye should not be admitted in unrestricted quantities. In this way you stimulate efficiency in a way which bounties and subsidies will never do. There are many details to safeguard maker and user into which time will not permit me to enter to-night, but I trust I have said enough to convince the Committee that urgent action is needed and that a system of licensing modified as described is the least objectionable method which can be adopted."

THE CHEMICAL COMPOSITION OF TWO PALM TREE SEEDS OF MADAGASCAR.

THESE two trees belong to the West of Madagascar. One of them, the *Satranamira*, is the *Hyphane Shatan*, growing in the sedimentary basin and only disappearing in the Far South. The other, the *Dimaka*, is the *Borassus Madagascariensis*, common principally in the fertile alluvial plains of the river banks.

The *Dimaka* sample studied was in form of fragments of seed with a white fracture and sharp edges. Hardness of the albumen recalls corozo.

Satranimira seed is smaller than that of the *Dimaka*, and combines the hardness of corozza with very great elasticity, so that it can withstand the effects of violent impact without breaking.

Analysis of the two seeds gave:—

	<i>Borassus</i> . Per cent.	<i>Hyphane</i> . Per cent.
Humidity	10.25	12.10
Fats	0.51	8.08
Nitrogenous matter ...	4.84	5.95
Soluble Ash	1.20	1.01
Insoluble Ash	0.54	1.38
Cellulose	82.66	71.48
	100.00	100.00

The great difference in the percentage of oil will be immediately noted. The small quantity of fats, 0.51 per cent, from the ether extract from the *Borassus*, was in form of a red elastic pellicle of uniform aspect.

The *Hyphane* extract, on the contrary, gave a more abundant oil, 8.08 per cent, pale yellow, liquid at first, and then partially solidifying at 20° C. to form a mixture of buttery consistency with the odour of palm oil.

The iodine index of this oil is 21.9, and that of saponification 245.3. These values are sufficiently close, for the iodine index, of palm oils (13 to 14) and more, and of cocoa-nut (8 to 9).

The total sugars were estimated by the G. Bertrand method, and mannose by precipitation of the hydrazone mannose in acetic liquor, the precipitate being collected on a Gooch crucible. The glucose is determined by difference.

Cellulose of *Borassus* Seed.

	Weight of Sample. 30 Grms.	Residue.	Residue.
Total Sugars	13.550	3.140	2.355
Mannose	10.910	2.539	1.832
Glucose	2.640	0.601	0.523
Ratio Mannose Glucose	4.13	4.20	3.50

Cellulose of the *Hyphane*.

	Weight of Sample. 10 Grms.	Residue.
Total Sugars	3.435	2.450
Mannose	2.470	1.762
Glucose	0.965	0.683
Ratio Mannose Glucose	2.56	2.56

As for the percentage of nitrogenous matter in these two seeds, it is necessarily slight, considering the enormous proportion of carbohydrates. It is perceptibly the same in the albumens of the *Borassus* and *Hyphane*, which finally differ mainly by the greater richness of the seed of the *Hyphane Shatan* in fats, and as regards cellulose by predominance of the products of condensation of mannose over those of glucose in the seed of the *Borassus Madagascariensis*.—*Bulletin du Musée Colonial de Marseille and Les Matières Grasses*, October, 1920.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

November 12, 1920.

Prof. Sir W. H. BRAGG, F.R.S., President,
in the Chair.

"Ionisation and Excitation of Radiation by Electron Impact in Helium." By Dr. F. H. GOUCHER.

Measurements have been made of the critical potentials for helium by the method used in the experiments of Davis and Goucher, these being compared with the ionising potential of mercury vapour taken as a standard.

Assuming the ionising potential of mercury to be 10.4 volts, two critical potentials occur in helium. One at about 20 volts and the other at about 26 volts. These critical values agree well with those obtained by Horton and Davies.

The effect of radiation alone on the metal parts of the apparatus was studied under conditions which would yield evidence of use in the interpretation of the results obtained when the production of both ionisation and radiation was taking place simultaneously.

The conclusion was reached that the lower critical potential was a radiation potential, though some ionisation was produced also at this potential. This, however, was attributed to the presence of impurity, probably hydrogen. The higher critical potential was that at which ionisation took place.

DISCUSSION.

Mr. B. S. GOSSLING discussed at some length the effect of impurities on the lowering of the ionisation potential, illustrating his remarks with curves shown on the screen. A full account of his remarks will appear in the *Proceedings*.

The PRESIDENT asked if argon behaved in a similar way to helium as regards the effect of impurities.

Mr. GOSSLING mentioned that Stead's values for argon were also low, but whether this was due to impurities or not he could not say.

The PRESIDENT asked if these critical potentials corresponded to the production of lines in the spectrum of the gas.

Dr. GOUCHER said the radiation potential did correspond to a line. In mercury for instance, the radiation potential was 4.9 volts, which, as McLennan had shown, corresponded to the production of a single line in the mercury spectrum. The many-lined spectrum was produced when the potential was at or above the ionisation potential. He thought Mr. Gossling's curves were of considerable importance.

"The Location of Interference Fringes." By Mr. J. GULD.

The Paper treats of the conditions under which interference fringes, produced by reflection of light from the two surfaces of a "thick plate," are visible to an observer. The treatment lays stress on the physical significance of the term "location" as applied to interference fringes, and the dependence of the observed phenomena on the conditions of observation. For a broad source of light a formula is obtained which is equivalent to that derived by Michelson. For a joint source of light at infinity, it is shown that the fringes obtainable are equally visible at all distances from the plate.

"Fringe Systems in Uncompensated Interferometers." By Mr. J. GUILD.

The Paper mainly consists of an investigation of the form of the fringe system observable at infinity, or in the focal plane of a telescope, when a broad source is employed with a Michelson interferometer, in which the glass paths of the two interfering beams are not equal. The fringes may be elliptical or hyperbolic, with circles and straight lines as special cases. In the recently developed method of using the instrument for optical testing, the fringes due to a joint source at infinity are employed. It is shown that the form of the fringes in this case are unaffected by lack of compensation, but that the visibility of the fringes is conditional by the nature of the fringe system due to a broad source.

DISCUSSION.

Mr. F. TWYMAN, of Messrs. Adam Hilger, Ltd., made a written communication which will be published in the *Proceedings*.

"A New Relay for Heavy Currents." By Dr. GUY BARR.

The action of the relay depends on the fact that no arc can be maintained between mercury electrodes in hydrogen. One lead is brought to mercury contained in a vertical tube within a solenoid. An iron rod, at the upper end of which is a glass cup, floats in the mercury. The cup also contains mercury, and the other lead is connected to an iron rod which dips into this. When no current flows in the solenoid, the rim of the cup is about 1 cm. above the level of the main body of mercury. When the relay current (about 0.03 ampere) is running the iron rod is sucked down until the rim of the cup is submerged by about 0.5 cm. The space above the mercury contains hydrogen. The relay can be used to break quite large currents (20 amperes) without much spark.

DISCUSSION.

Mr. C. C. PATERSON asked on what voltage the apparatus would work, as the energy in the spark would depend on this.

Dr. BARR said he had not tried it above 100 volts.

Mr. F. E. SMITH suggested as a simplification that a U tube might be employed, in one limb of what was the iron float. When this was sucked down the rising mercury in the other limb of the U could make connection between two iron electrodes.

Dr. BARR said it was important that the break should take place between mercury surfaces, otherwise the mercury got contaminated.

Mr. GUILD suggested that if the mercury in the second limb of the U were made to flow over and make connection with some stationary mercury in a side tube the difficulty of Mr. Smith's arrangement would be overcome.

Mr. PATERSON asked how hot the apparatus would get if the current were broken as frequently as, say, 10 or 20 times per minute.

Dr. BARR replied that he had not had occasion to try it as rapidly as that.

Dr. HOPWOOD asked if the break was "clear," or if the oscillations set up in the mercury were sufficient to make and break the current after the first break had occurred.

Dr. BARR said there was no evidence of this. There was very little disturbance of the mercury in actual practice.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

L'Age de Fer, October 25, 1920.

TITANIUM AND ITS INDUSTRIAL APPLICATIONS.—Georges Carteret—Titanium is extracted mainly from two ores—rutile and ilmenite. Rutile is mined in Norway, America, and Australia. New deposits have been discovered in Africa, in Dahomey, Nigeria, Gold Coast, and Madagascar. Ilmenite (FeTiO_3 or $\text{TiO}_2 \cdot \text{Fe} + \text{Fe}_2\text{O}_3$) is not so rich in titanium as rutile, but it is more abundantly found. It is found in Russia and in Norway. Also there are important deposits in Senegal (Africa), Java, Canada, and New Zealand. The island of Madagascar also contains important deposits of ilmenite, which have not been up to the present much exploited. M. Auclair, controller of the mines at Vongoebe, discovered in 1912, estimates that the deposits in Betsirivry alone will yield 3,500,000 tons of iron rich in titanium, to the extent in certain specimens of 40 per cent titanic acid. Great difficulty was first experienced in the preparation of metallic titanium. Berzelius obtained it by treating potassium fluotitanate with potassium. Titanium has a great affinity for nitrogen, and these crystals were first taken to be metallic titanium. Metallic titanium is now obtained by reducing rutile by carbon or aluminium in the electric furnace. Purification is effected by re-melting in the electric furnace in the presence of titanic acid. The uses of titanium include its use as a white pigment for painters, its alloys with iron being very important. During the war, the tetrachloride of titanium was successfully used for making white smoke clouds.

NOTES.

AN ALLEGED ALLOTROPIC FORM OF METALLIC LEAD.—About five years ago it was observed by H. Heller that compact metallic lead, when placed in contact with acidified solutions of lead salts, undergoes after a time a remarkable change, becoming filled with cracks at first and finally falling to powder. It was concluded that an allotropic form of lead was thus produced, similar to the well-known change of ordinary tin into the grey modification. This view was confirmed by Cohen and Helderman, who studied the phenomenon by means of the dilatometer; they believed that no chemical reaction took place, and decided that the allotropic form was more dense than ordinary lead. A. Thiel has now studied and discussed this matter very thoroughly, and has reached the conclusion in a very convincing way that this is no case of allotropy at all, but a peculiar case of chemical action. He finds that the action takes place only when lead nitrate is present in the solution, and that a well-known chemical reaction takes place, dissolving the lead with the formation of lead nitrite. The peculiar action throughout the mass of the metal is explained by Thiel as due to the presence of a more readily attacked eutectic existing between the original crystals of the metallic lead. The arguments are very convincing, and it appears that the powder is certainly not an allotropic form of the metal.—*Berichte*, lxxiii., 1052.

ROYAL INSTITUTION.—A General Meeting of the Members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Prof. J. Perrin (Paris) and Prof. C. Fabry (Marseilles) were elected Honorary Members; and Mr. A. C. Chapman, Mr. N. D. Grinké-Drayton, Mr. W. J. Hemp, Mr. C. H. Nash, Mrs. L. Pennington, Dr. J. Taylor, Mr. J. S. Weir, and Mr. R. E. Winkfield were elected Members. Dr. Arthur Keith was re-elected Fullerian Professor of Physiology for a further term of three years. The Lecture arrangements for the coming Session were announced. The Christmas Course of Juvenile Lectures this year will be delivered by Prof. J. Arthur Thomson on the "Haunts of Life," commencing on Tuesday, December 30 with the School of the Open Shore; followed by the Open Sea; the Great Deep; the Freshwaters; the Conquest of the Land; and the Mastery of the Air.

MEETINGS FOR THE WEEK.

Monday, December 13.

Royal Society of Arts, 8.
Faraday Society, 8.15. Dr. A. E. Oxley will present a Paper by Prof. E. D. Campbell, (Michigan), and open a Discussion on "A Force Field Dissociation Theory of Solution applied to some Properties of Steel."
"Electrical Resistivity of Dilute Metallic Solutions" by A. L. Norbury.
"The Forms of Electro-deposited Iron and the Effect of Acid upon its Structure" by W. E. Hughes.
(The Annual General Meeting will be held at 8 p.m., before the Ordinary Meeting).

Tuesday, December 14.

Institution of Petroleum Technologists, 5.30.
Institute of Metals, 8. (At Glasgow and Birmingham).

Wednesday, December 15.

Royal Society of Arts, 4.30.
Conjoint Board, 5.
Institution of Electrical Engineers, 6. (Wireless Section).

Thursday, December 16.

Society of Chemical Industry. (At Birmingham).
Institution of Mining and Metallurgy, 5.30.
Institution of Electrical Engineers, 6.
Chemical Society, 8.

Friday, December 17.

Institute of Metals, 7.30. (At Sheffield). :

NOTICES.

EDITORIAL.—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

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TEMPERATURE MEASUREMENTS IN STEEL FURNACES.*

By GEORGE K. BURGESS

Chief, Division of Metallurgy, Bureau of Standards,
Washington D.C.

FOR several years past, the Bureau of Standards has been actively interested in some of the fundamental problems related to the steel industry, especially subjects of a scientific or technical nature. Among those with which I personally have been engaged, is the question of temperature measurement as applied to the various stages of steel manufacture. The particular phase of this subject, that of the measurement, control, and interpretation of the temperatures of the masses of steel during its manufacture, and while the metal is still liquid, is, perhaps, the most difficult temperature domain to conquer, as it is likewise the most important from the economic point of view.

May we not state as an axiom that in a basic industry, if there is a factor such as temperature of the operations or materials, which is generally felt to play a capital role, limiting in an as yet undetermined way, the quality, output, and cost of product; then, in such cases all reasonable effort should be devoted to ascertaining the effects of the factor in question.

That every steel maker is convinced of the importance of adequately defining quantitatively the role of temperature in the various stages of steel manufacture, I think, would be readily conceded; but is it not also true that no steel manufacturer can state for liquid steel other than in vague terms if at all, the relation of temperature at each stage of the process of melting, refining, and casting, to any of the other factors influencing his product?

There have been a number of papers published lately, particularly by the Iron and Steel Institute of Great Britain, treating of the processes of steel manufacture, and in most, if not all of them, particular emphasis is placed on the role of temperature; but in none of them, apparently, does there appear, for the stages of the process while the steel is still within the furnace, statements of the relations of temperature to other factors backed up by satisfactory, quantitative measurements of temperature. This situation exists in spite of the fact that for many years there have been available pyrometric instruments adequate for use in the steel industry. The reason for this anomalous condition appears to lie largely in the fact that more than a pyrometer is needed.

As to the pyrometer, it is of interest to note that the demand for an instrument to measure temperatures of liquid steel came from the steel industry itself; and at the time, in 1892, when Sir Robert Hadfield requested M. LeChatelier to devise a suitable instrument, there was no existing type of pyrometer adapted to this purpose. The genius

of LeChatelier, and the skill of the French optical firm, Pellin, produced the LeChatelier pyrometer, not to be confused with the thermoelectric instrument, also known as the LeChatelier pyrometer.

It was reserved to an American, E. F. Morse, to invent, in 1902, the most convenient type of pyrometer for use in measuring the temperatures of liquid steel and other incandescent and inaccessible objects; this pyrometer has since been simplified and improved by others. It is again not without interest to note that the steel industry itself furnished the basis for this invention, which was an improvement of a method invented by Messrs. Taylor and White for use in controlling the temperature of certain hardening baths at the Bethlehem Steel Company's plant.

In the portable form with tripod, the type I personally prefer, or in that manufactured by Leeds and Northrup, which is generally used, in which no tripod is required, the brightness of a small incandescent lamp at the focus of a telescope is matched in brightness against the incandescent background of the liquid steel or other hot object. The electric current taken by the lamp gives a measure of its temperature and thus also of the steel if certain very important conditions are also fulfilled.

The consideration of these all important accessory conditions brings us to a phase of the subject in part illustrated by what has gone before, but which may, perhaps, best be emphasised here; namely, for the solution of problems of this kind, there is generally required the co-operation of some three types of individuals, the steel maker who best knows his problem; the scientific man, or, if you prefer, the research laboratory, who can bring the application of abstract principles and methods of measurement to bear on the problem; and last the instrument maker who can put in concrete and sufficiently robust form the ideas of the scientific man that best meet the needs of practice.

At the remarkable symposium on pyrometry held in Chicago recently under the auspices of the American Institute of Mining and Metallurgical Engineers there were papers relating to steel manufacture by these three types of men. Such an interchange of viewpoint and experience makes for progress. It was made evident by this symposium, however, that although there have been developed satisfactory instruments for measuring temperature in open-hearth and electric furnaces and of liquid steel streams; and there have been made sufficiently exact determinations of the underlying physical facts and phenomena on which such temperature measurements are based; and also there has been accumulated a considerable mass of experimental data relating to furnace operations by various observers; and above all, there has been unquestionably established a most splendid spirit of confidence and co-operation among the three types of men mentioned above; nevertheless, it is only fair to state there yet remains to be solved the essential kernel of the problem, namely, the actual, quantitative relations existing between temperature and the other factors relating to steel manufacture.

As illustration of the role played by the research laboratory in this problem of temperatures of liquid steel, let us take the determination of the corrections to be applied to the optical pyrometer

* Read at the Fifteenth General Meeting of the American Iron and Steel Institute, New York, October 24th, 1919.

such correction arises from the well-known fact readings to give true temperatures. The need of that the intensity of total and also of monochromatic radiation of any substance, not enclosed within a furnace uniformly heated, depends not alone upon its temperature but also upon the nature and character of the radiating surface. It then becomes necessary in the case of liquid iron, steel, oxides, and slags, for example, to find their emissivity or specific radiation for the coloured light used with the pyrometer. This can best be done in the research laboratory and not in the steel plant. This fact needs emphasising as it has sometimes been said, the research laboratory of a steel plant should be the steel plant itself. I believe it will be found, as in this instance, that the plant itself does not, in general, provide the facilities and material adequate for the determination of fundamental constants and properties.

Thus, we spent considerable time in various steel plants trying to determine the radiation characteristics of liquid steel but with unsatisfactory results. The actual determinations were made in the laboratory with an instrument we have devised which is identical in principle with the optical pyrometer above mentioned except that it was a microscope instead of a telescope, and the masses of steel operated upon, instead of being 50 tons or more, were of the order of a few thousandths of a milligram. With the micro-pyrometer, as we call it, we were able to show that the emissivity or specific radiation of pure iron is 0.37 with light of wave length, $\lambda = 0.65 \mu$ (*i.e.*, for red light used with the pyrometer, a free surface of iron radiates only 37 per cent of the same light from a furnace at the same temperature as the iron); furthermore, this quantity ($e=0.37$) remains constant over the whole temperature range of steel manufacture and is not altered by the presence of any of the elements which may be present in steel and iron, and is also nearly identical with the emissivity of nickel and even, as very recent measurements show, of monel metal and other alloys of iron or nickel so long as they show no change in colour caused by alloying. Similar measurements were made for iron oxides in liquid and solid states and of slags. It was then a simple matter to construct correction tables for the pyrometer when sighted on any of these substances. (In steel manufacturing practice it was found advisable to adopt the value 0.40 rather than 0.37 for iron and steel and the correction tables are based on the $e=0.40$ for $\lambda=0.65 \mu$, for reasons explained in the Bureau of Standards Technologic Paper 91, published 1917).

As there is a mass of data which has been gathered on measurements of steel temperatures by the ever-increasing number of observers, it is not my intention to go into detail here. They are available or referred to in the papers of the Chicago Symposium. It may, nevertheless, be well to summarise here the present state of the subject.

The Pyrometer Committee of the National Research Council, among others, have made an extended survey of the possibilities of various methods of measurement of liquid streams of iron, steel, and slag, and of temperatures in open-hearth and electric furnaces.

The question of measuring accurately, most conveniently, and practically instantaneously, or to

better than 5° at 1500° C. (2732° F.) in intervals of 5 to 10 seconds, the temperature of running streams of liquid steel, as in tapping a furnace or teeming ingots, may be said to have been solved some time ago by the use of the above described optical pyrometer of the modified Morse type, to the readings of which corrections are to be applied based on $e=0.40$ for $\lambda=0.65 \mu$ when sighting on iron or steel with similar corrections for liquid iron oxide ($e=0.53$) and slag ($e=0.65$ or thereabouts depending somewhat on the nature of the slag). This does not mean that other pyrometers cannot be used successfully for this purpose, for they have been, including other types of optical pyrometer and various total radiation instruments.

It has been demonstrated also that the arch or dome of an open-hearth furnace may be watched and its temperature controlled by the same pyrometer, although here no corrections appear to be necessary to the observed temperatures.

Similarly, the temperature of the surface of the slag in an electric or open-hearth furnace may be observed through peep holes with doors shut if care is taken to avoid flames and smoke; and the progress of the heat as related to slag temperatures may be followed with considerable accuracy at least for open-hearth furnaces.

The most difficult and most important problem is to determine, for any instant of time and condition of bath, the temperature of the metal bath itself. There is perhaps, some comfort in appreciating that, in general, this difficulty is offset in part by the fact of non-uniformity of temperature within the metal unless the bath is well and frequently stirred. These differences within the bath, as have been shown from a series of observations of tapping temperatures, may reach under certain methods of operating, 200° F. or more and are evidently within the control of the melter.

Considering the apparently crude methods in use, it is a source of wonder to anyone who has had occasion to check the temperatures of steel, as cast, to note the marvellous uniformity attained from one heat to another by the furnace men. For example, the method of timing the appearance of crust in the chill test as often used appears to have no necessary relation to the bath temperature; nevertheless, this remarkable uniformity in casting temperatures extends over the whole steel industry.

The Pyrometer Committee, above-mentioned, made a series of trials of an improved form of the chill test, devised by Mr. Drinker, and were reluctantly forced to the conclusion that reliable estimates of bath temperatures cannot be obtained by this method. All methods, which depend on lifting out metal from the furnace in a spoon, are subject to so many sources of error and require such rigid exactness of manipulation as to be unsuitable for ordinary practice and of doubtful reliability even when extraordinary care is exercised, although there have undoubtedly been made excellent individual observations by such methods.

An elaborate series of experiments were carried out by the Committee with various refractory tubes thrust into the metal bath; but, with the exception of the single substance, Acheson graphite, no material was found satisfactory. In this procedure the optical pyrometer is sighted down the tube on the closed end of graphite immersed in the bath to the desired depth. More surveys

should be made by this method using graphite tubes. Pieces of graphite or graphite tubes may also be plunged into and held beneath the surface of the bath in electric and open-hearth furnaces and then allowed to come to the surface or removed from the furnace entirely, and the temperature of the metal at any depth may then be estimated quite accurately in either case from observations taken with the optical pyrometer of the graphite temperatures. No corrections have to be applied to the instrument sighted on graphite, and this graphite has the further advantage that slag does not stick to it.

The question of following electric furnace temperatures is complicated by the presence of the electrodes, but the practice of changing slags gives opportunity for intermittent temperature observations of a satisfactory nature by various methods as shown by Mr. Bash in a paper presented at the Chicago Symposium. The technique of electric furnace temperatures, however, needs considerable additional study. From a comparison of casting temperatures of several electric and open-hearth furnaces in normal operation, Mr. Bash concludes that electric furnaces are not tapped at higher temperatures than are open-hearth furnaces, as is often held.

It would appear that heretofore most of the determinations of furnace temperatures have been made by representatives of the research laboratory or instrument maker, and nearly all the published observations were so taken, although there is undoubtedly in existence considerable data and experience accumulated by steel makers themselves. It is evident that discontinuous observations taken somewhat casually by outside parties, although they may serve excellently for demonstration purposes, can nevertheless by no means replace the continuously carried out observations made by representatives of the steel maker himself over long periods of time and under the incessantly changing conditions of practice. In this way alone can the problems of temperature conditions, control and interpretation be solved.

There has been furnished the steel maker for this task, a simple, accurate, and convenient pyrometer; the technique surrounding the taking of steel furnace temperatures has been sufficiently, if not definitely worked out; and there have been determined all the fundamental physical constants necessary for transposing the observational readings into actual temperatures. The steel maker himself will have to solve the rest of the problem.

THE ORIGIN OF PRIMARY ORE DEPOSITS.*

By J. MORROW CAMPBELL.

(Continued from p. 282a.)

By the absorption of water, basaltic magma probably yields diorite as the acid fraction and a residue of peridotite. The latter in turn, when further acted on by water, is converted into serpentine giving up silica, which appears as quartz or chalcidonic veins in it and the surrounding sediments. The still further action of water is to break up the silicates completely and leave a residue of chromite, ilmenite,

or magnetite almost free of silica and so different from magmatic material in general that their igneous origin has been seriously questioned.

Concerning the solvent power of the mother-liquor from granite there can be no possible doubt. The view now advanced is that this power is due to silicic acid. It provides the only rational explanation of the segregation of the granitic constituents from the primary magma, and, with them, the ore minerals.

The amount of ore minerals dissolved out of the primary magma must depend upon the amount present in it, the amount of free silicic acid and the degree of solubility of the ore minerals in silicic acid. The metals gold and bismuth appear to be freely soluble, also cassiterite and tungstic oxide. Of the sulphides those of molybdenum and bismuth seem the most soluble, followed by pyrites, chalcopyrite, arsenopyrite, stibnite, galena and sphalerite. Platinum is insoluble, chromium oxide nearly so, and titanium oxide sparingly soluble. Fluorides and boric oxide are freely soluble as well as the rare earths, niobates and tantalates.

The basic fraction retains only the residue of ore minerals not dissolved by silicic acid in the acid fraction. Most of these appear to segregate in the molten condition previous to the crystallisation of the silicates, sink and coalesce. Magnetite and ilmenite crystallise out before the silicates, and in many cases remain disseminated through them.

The question of penetration of the crust of the earth by water is one which has caused much controversy, but it must be admitted that water can and does reach great depths, for example through fissures produced by earthquakes—it would be folly to deny the possibility of this.

If the theory here advanced is the true explanation of magmatic segregation the rarity of the non-siliceous rocks demonstrates how seldom it is that water reaches magmas in sufficient quantity to produce its final result; also that its infiltration is local in nature. Incidentally it also proves that there cannot be any reservoir of water in magmas; if there were, ultrabasic rocks should be abundant.

To summarise:—This theory of magmatic differentiation requires the presence of water. It is absorbed by the magma entering into combination with silicates as hydroxyl, and setting free bases, the affinity of which for silica is not very strong. Some silicates are broken up yielding free silicic acid which in turn forms a solution with aluminosilicates, especially those containing potash, which are readily soluble in it. This acid solution next segregates, and on cooling yields granite, syenite, diorite, etc., depending on the nature of the primary magma that has been leached. The acidic extract previous to solidification may absorb other rocks in contact with it, undergoing in this way considerable modification in composition—the higher the temperature the greater may be such change. The leaching of a basaltic magma might therefore yield quite a variety of rocks; the remainder, however, would be ultra-basic and contain much residual ore mineral. In the presence of carbon or carbon monoxide metallic iron would be produced. The presence of metallic copper in basic igneous rock is probably due to a similar cause.

*From Bulletin of the Institution of Mining and Metallurgy, October, 1920.

In Burma considerable areas of serpentine occur in which native copper and chalcocite are associated with chromite. The conditions under which the copper ores occur lead to the belief that their formation was contemporaneous with serpentinisation. Their formation was contemporaneous with serpentinisation. Their deposition coincided with the period of ejection of the acid extract of the original peridotite. This acidic material is to be seen now in veins traversing the serpentine in the form of coarse quartz-hornblende pegmatite, and also chalcocitic quartz veins. At its periphery it is common to find a band of highly feldspathic rock, evidently an acidic differentiate—the result of a previous leaching: the origin of this was evidently prior to that of serpentinisation. This serpentine occurs in the midst of Cretaceous rocks, and beyond the periphery very numerous fissures in the sediments are filled with crystalline quartz. There is no granite or other igneous rock in the vicinity.

These phenomena helped to confirm the writer in the opinion that differentiation is brought about by absorption of water.

The matter of differentiation by means of fractional crystallisation within a basic or ultra-basic sub-magma does not come within the scope of this paper.

The Ore Minerals of Acid Magmas.

Magmas are here called acid which on solidification yield free silica, and all water present in acid magmas is regarded as being combined as hydroxyl with silica or silicates. Silicic acid is believed to be the solvent of the granitic as well as the ore minerals. The latter must be the more soluble since they crystallise out at a later stage and at a lower temperature than the bulk of the silicates.

Since the theory here propounded traverses the pneumatolytic theory we shall consider the merits of the latter at once.

(a) *Pneumatolysis. High Temperature Ores.*—The ore minerals which develop first from the mother-liquor are molybdenite, cassiterite, tungstates, metallic bismuth and bismuthinite. Since they so frequently occur in intimate association with one another it is reasonable to suppose them to be homogenetic or of similar mode of origin. If one is of pneumatolytic origin probably they all are. We shall take tin and tungsten as typical of the group. The minerals containing them have been accepted for fifty years as being of pneumatolytic origin, that is, they are supposed to have been present in the magma as fluorides, and to have been given off in the gaseous state along with water above its critical temperature.

If tin and tungsten were present as fluorides in the primæval molten crust it is difficult to understand why they were not expelled as gases. If they were not, it is hardly credible that they could have been given off as gases from magmas at a lower temperature and much greater pressure. Tin fluoride with a boiling point of 705°C . possibly might have been retained, but it would be impossible in the case of tungsten fluoride with a boiling point of 19°C . at 760 mm. pressure.

Even if they were retained and subsequently given off on the cooling of the granite magma let us investigate the conditions of their expulsion. A gas in solution is expelled owing either to the

freezing of the solvent or to release of pressure. The former cannot be the cause, for the ores are found solely at the granite periphery—an impossible position, since granite solidifies from the surface downward. Next, release of pressure is not the cause, for, if it were, we should find tin and tungsten ores exclusively at the highest points on the periphery; gas liberated from solution would undoubtedly collect there. These ores are found only at and near the periphery of batholiths, but not by any means exclusively or invariably, or even usually at the highest points.

Pneumatolysis demands that water be present with fluorides, but there is no evidence that water in the gaseous state is either present in a granite magma or given off by it.

The difference between the boiling points of tin and tungsten fluorides at atmospheric pressure is nearly 700°C . Within a magma pressure will certainly raise the boiling point of both, but the difference between them under any conditions is likely to exceed 300° . If the difference were only 100° it is still far too great to permit the possibility of cassiterite and tungstates being developed from the fluorides in contact with one another and practically simultaneously.

The observed phenomena of cassiterite veins in sedimentary rocks proves most conclusively that the walls were not subjected to a temperature exceeding 700°C ., to which they certainly must have been exposed if tin were introduced between them as fluoride. The boiling point of SnF_4 at magmatic pressures must be considerably over 700°C .

It is thus seen that the evidence on which the pneumatolytic origin of cassiterite is based all breaks down when analysed.

Next, let us consider the value of the evidence which tourmaline is supposed to give in support of the pneumatolytic theory.

Tourmaline has never been synthesized. It is supposed to be the result of fumarole action, but this is by no means certain. Its companions are biotite and muscovite, both containing hydroxyl and not of gaseous origin. Because certain substances are given off as gases at the surface it does not follow that they are given off as such by magmas. Tourmaline occurs in association with gold, pyrites, hematite, chalcocopyrite, and tetrahedrite just as fluorite, another common associate of cassiterite and tungstates, is also a common associate of galena. None of these ore minerals is of pneumatolytic origin, therefore the association of either tourmaline or fluorite with ores has not the genetic significance that is usually ascribed to it.

Both tourmaline and topaz alter to mica; this proves allied molecular structure, and indicates a mode of origin similar to that of the micas.

Such is the evidence upon which the pneumatolytic theory of the genesis of the high temperature ores is based. We regard it as so unsatisfactory that the theory must be abandoned.

The fact that tin has been reported so frequently as present in traces of hot natural waters and in the solids deposited from them, combined with the fact that tin oxide sometimes enters into the composition of silicates, leads us to believe that tin certainly exists in silico-aqueous solution. That tungsten can be carried in a similar solution is proved by the fact that silico-tungstic acid and its alkaline salts are readily soluble in water and

stable to over 350° C. at atmospheric pressure and probably to a much higher temperature at magmatic pressures.

Quartz is the invariable companion of both tin and tungsten ores, and the importance of this fact seems to have been overlooked.

The evidence in nature is overwhelmingly in favour of tin and tungsten having been transported in a silicic acid medium and deposited therefrom probably by loss of heat, the same solution depositing quartz either simultaneously or at a later stage.

(b) *Gold*.—In primary gold deposits quartz is always present.

We also have quite satisfactory evidence that, in some cases at least, gold and quartz have been deposited simultaneously from the same solution.

Maclaren (J. Malcolm Maclaren, "Gold," 1908, p. 39) refers to silicate of gold, and indicates its possible importance in nature. Twelve years ago, however, he regarded alkaline sulphides as the principal carriers of gold. That secondary enrichment may be due very largely to the action of this solvent is probable, but there appears to be much more evidence in support of the belief that silicic acid was the vehicle that translated gold from magmas to veins.

The function of silicic acid as a solvent of gold may not be confined, however, to magmas. It is well known that no extensive auriferous alluvials have been found in either Mesozoic or Palaeozoic rocks. No one is likely to argue that such never existed. We must assume that such were deposited and that the metal has been removed by some means in solution. At the same time we must recognise that in most cases gold has not been leached out of Tertiary alluvials. What solvent is there in nature that could remove gold at great depths and not at shallower ones? It is apparently a matter of temperature and pressure. We argue that silicic acid is the solvent. It develops only at high pressure and somewhat elevated temperature, and all the older rocks must have been subjected to its influence, whereas it is only rarely that Tertiary rocks have been buried to a sufficient depth for it to have formed in them. It is difficult to find any other natural agent sufficiently abundant that would be capable of dissolving gold out of deep-buried alluvials and of leaving it in shallower deposits.

That siliceous water carries gold is well known; it has been found in several places in siliceous sinter deposited by such water. This strongly supports the present hypothesis.

(c) *The Base Metals*.—With primary ores of copper, zinc, lead, and antimony, we are faced by the same fact that in the veins along with them quartz is almost always present.

There is good reason for believing that the sulphides of these metals came up from magmas in silicic acid solution. The mode in which they were dissolved or combined during their liquid phase is not evident, but the writer favours the idea that it is a case of combination rather than of simple solution. A parallel to the silicate-sulphide molecules that are assumed to be formed is found in lapis lazuli. In this the mineral lazurite is a double silicate-sulphide of soda and alumina, assumed, on account of its analogies, to consist of double silicate of soda and alumina combined with double sulphide of soda and

alumina. It is quite reasonable to suppose that at high pressures sulphides of the heavier metals may combine in compound silicate molecules and be expelled again at reduced pressures.

Silicates at magnetic temperatures and pressures and in the presence of the elements of water, take up fluorine, boron, &c., as in topaz and tourmaline. There are good grounds for the belief that these and many other minerals formed in similar situation, crystallised out of silicic acid solution.

(d) *Ore-bearing Solutions, Concentrations, &c.*—Literature dealing with the genesis of primary ores is very vague as to the conditions of solution or combination in which they are transferred in nature.

For tin there has been the pneumatolytic theory, but for other metals we have little more than the very unsatisfying statement that "ascending hot waters" were the transporting agent.

It is not considered necessary to review the various theories put forward regarding the sulphides of copper, zinc, lead, and antimony, or those dealing with native copper. Various substances have been regarded from time to time as solvents and reactions in the form of chemical equations have been given as explaining various phenomena, but the weakness of all these is that they disregard the simultaneous presence of quartz. They also assume in too many cases the presence of substances in magmatic liquids the very existence of which under such conditions is problematical, the presence of which can be only fortuitous, and which are certainly unessential. It appears that, too frequently, solvents, which no doubt are of great importance in leaching ores and in secondary enrichment, are given credit for primary functions really performed by silicic acid.

It is necessary to make a clear distinction between primary and secondary ores. This is specially important in the case of copper, where we find large quantities of secondary chalcocite deposited in veins enriching primary copper ores, or transported considerable distances and deposited in sedimentary strata, often replacing carbonaceous matter. The usual conspicuous absence of quartz in such deposits demonstrates that silicic acid is not the carrier of chalcocite.

Regarding the concentration of the solutions from which primary ores are deposited, similarly, the literature gives us very little assistance, and only sparse information is tendered as to the probable length of time occupied by the process of filling a vein. These are both considerations of some importance, and it is believed that nature furnishes data from which we can make reliable deductions.

Let us take the evidence of tin and tungsten ores.

Considerable masses of granite at the periphery of batholiths are known to contain cassiterite and wolfram as primary minerals. These are regarded as having been present in concentrated silicate solution, and that, owing to this concentration combined with rapid cooling, the ore minerals were unable to leave the magma before solidification. In such cases it is notable that overlying sediments have not undergone an appreciable amount of contact metamorphism and that, though the magma at greater depths discharged mother-liquor through fissures in the granite that extended into the overlying sediments, the veins

in the former always but in the latter rarely carry ores. Usually these solutions are sufficiently dilute and hot to escape on consolidation of the granite.

Pegmatite in veins usually merges by degrees into practically pure quartz, but quartz veins carrying cassiterite or wolfram are only rarely if ever quite free from mica. The siliceous solution, which deposits the ore minerals, on passing up vein fissures in granite causes greisenisation, *i.e.*, it converts potash feldspar into muscovite. This change involves the taking up of hydroxyl and the loss of silica. Incidentally, also fluorine is often taken up and ore minerals deposited, but these latter processes should not be, though they sometimes are, regarded as an essential part of greisenisation. True greisens very often contain neither fluorine-bearing nor ore minerals.

It is extremely unlikely that a dilute solution could cause greisenisation.

Pegmatites are known consisting of over 50 per cent of ore minerals: molybdenite, bismuthinite, wolfram, scheelite, and pyrites, with mica and quartz. The solution that deposited this mixture must have been very concentrated, and, moreover, the process was completed in all probability in a very short space of time—days rather than years.

We do not know with certainty what was the immediate cause of fissuring, but the indications point to very rapid action and the practically instantaneous filling of fissures by mother-liquor as a concentrated solution which deposited its ore minerals very rapidly when the temperature and other conditions were congenial. The conditions that caused the first fissuring recurred in many cases and resulted in the reopening of the old fissures or the formation of a new series differing in orientation even to right angles. The high-temperature ore deposits furnish the best evidence regarding both degree of concentration of ore-bearing solutions and duration of the period of deposition. It must be borne in mind that ore-bearing solutions were in their most concentrated form when leaving the magma, and that they became more and more dilute as they passed upward. It is evident, therefore, that the high temperature ores were deposited from much more concentrated solutions than others. The indications are that these solutions in many cases actually approached saturation, if, indeed, they did not attain it on leaving the magma.

The conclusion arrived at tentatively is, therefore, that the mother-liquor when leaving the magma is a concentrated solution and that the ore minerals it contains are deposited from it rapidly as it ascends.

(e) *Temperature of Deposition.*—The temperature at which tin and tungsten ores are generally supposed to have developed has been regarded for some time by the writer as much too high. The temperature range also within which they are released from solution is believed to be much narrower than is usually accepted.

The opinion as to temperature of deposition appears to be confirmed by a phenomenon observed at Zinba wolfram mine in the Tavoy district of Burma, which probably gives a reliable indication of the approximate temperature at

which molybdenite and wolfram developed. In that mine it is not uncommon to find small masses of bismuthinite of rounded form enclosed in molybdenite, wolfram, fluorite, and quartz. The shape of these and their position demonstrates quite conclusively that they were introduced in the molten condition into the position where they occur. Since bismuthinite in its ordinary form is deposited at a lower temperature than molybdenite of wolfram and probably simultaneously with quartz (since it is often found in minute crystals scattered through the latter) it seems probable that these prills of molten bismuth sulphide separated out of solution in the magmatic liquid in the vein at a higher level than that where they are now found, and reached their present position by gravitation. Since the same mineral, at a slightly higher level (and presumably at only a slightly lower temperature), developed in normal solid crystalline form, usually in quartz, it follows that the molten prills referred to could not have been formed at a temperature much above the solidifying point of fused bismuth sulphide. The melting point of bismuth sulphide, in the vicinity of which it commences to dissociate at atmospheric pressure, is $^{\circ}\text{C}$.

The solidifying point of the fused mineral is probably a little lower, certainly not higher.

We may therefore regard the melting point of bismuth sulphide as the probable maximum temperature at which molybdenite develops and, since this mineral appears to form before either wolfram or cassiterite, the temperature at which the two latter commence to develop must be slightly lower.

The generally accepted cause of deposition of ore minerals in veins is falling temperature. Solutions are supposed to deposit, owing to progressive cooling as they pass upward, the various ores they contain at different levels in veins. There cannot be any real doubt that this is true in the main, but we have good reason for believing that there are other, probably contributory, causes. The various recorded phenomena of the occurrence of tin and tungsten ores in various parts of the world seem quite inexplicable if no factor but temperature operates in causing deposition. It is difficult to say what other cause there may be unless it is pressure, for our knowledge of the problem is as yet too scanty.

Similarly in the case of zinc and lead sulphides there is good evidence that the former usually develops at a higher temperature than galena, yet, in the greatest mines in the world yielding these metals, they have been deposited simultaneously.

There is another cause of primary ore deposition that must be mentioned, and that is the effect of substances encountered by ore-bearing solutions in the walls of the fissures through which they pass. This cause may be regarded as an accidental one, though from the economic point of view it is frequently of prime importance. Such information as we possess in this connection, sparse though it may be, is of considerable value.

Vein Fissuring.

In several respects the study of tin and tungsten-bearing veins, especially in Burma, gives valuable information regarding the production of the fissures these veins now occupy.

They usually occur in parallel series close to one another within circumscribed areas. These fissured areas are small, seldom as much as 2000 feet across, and circular or oblong in general outline. When they are in sedimentary rocks the ore-bearing zone is not usually over 300 feet in vertical depth, but may extend up as far as 1000 feet above the granite periphery, only the upper part being of any value. It has been proved that the ore-bearing veins, very numerous at the present surface, diminish greatly in both number and width at depth.

It is evident that this type of fissuring could be produced only by some expensive force in the magma—they could not possibly be the result of contraction. Since the total length of the fissures in many cases does not exceed the vertical distance from the surface to the granite periphery it follows that the causative force must have acted in only a very small area either at or very near the surface of the granite. The force obviously must have been of great intensity, and in all probability acted with almost explosive violence. There cannot be any reasonable doubt that the fissures referred to were opened up suddenly to their present width and remained open till filled. The theory that veins were opened up very slowly by the force developed by crystallisation of minerals in initially very narrow crevices is entirely unacceptable in the case of these veins. Frequently on the walls numbers of long, delicate, bladed crystals of wolfram are seen to have formed, and, without any interference with these, the remaining space was filled subsequently either wholly or only partly with quartz; in the latter case cavities are often lined with large quartz crystals. This condition of affairs is quite irreconcilable with crystal development having had any material influence in forcing the walls apart.

If we enquire more closely into the nature of the force causing fissuring we have to confess our ignorance. Goodchild's work has furnished the explanation most likely to be acceptable; the pressure consequent on the increase in solid specific volume of minerals in a cooling magma. The irresistible nature of this force and its development being coincident with the solidification of the magma meet the conditions as probably no other theory can. The amount of this expansion is so great as to far more than counterbalance the contraction that would otherwise result in the passage of granite from the liquid to the solid state. As it is operative throughout the whole of the freezing period in the granite, it is evident that its visible effects will appear in waves, so to speak. The upper portion solidifies first, and the bursting energy is stored within the magma, and appears to develop practically at its surface when the resistance of overlying rock is overcome, fissures are formed, occupied by mother-liquor and quickly filled with solids which seal them completely. Solidification of the magma proceeds downward, and more energy is developed which, finding no outlet, produces new fissures which may or may not coincide with the old ones, but occur in the same area. The fact that within the same circumscribed limits we have as many as three successive series of wolfram-bearing veins cutting one another proves that the first-formed fissures are filled rapidly and completely. Fissures of the second series are often similarly filled.

To be continued.

THE AMMONIA-SODA PROCESS.

By H. G. WILLIAMS.

A COMMON lecture experiment to illustrate the above is to pass CO_2 through strong AmOH saturated with NaCl . On examining a precipitate obtained thus, I was surprised to find it contained only about 30 per cent NaHCO_3 , and about 30 per cent NaCl , the remainder being apparently NH_4HCO_3 . On treating with CO_2 , a saturated solution of NaCl subsequently saturated with NH_3 , the precipitate obtained contained about 92 per cent NaHCO_3 . I can find no information on this point in any of the text books dealing with the Solvay process, which is of course carried out by the second method above. The alkalinity of the second solution was considerably stronger than that of the first, which would seem to make the formation of NH_4HCO_3 more likely. I shall be much obliged by any suggestions or information.

Robert Gordon's College, Aberdeen.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 25, 1920.

SIR J. J. THOMSON, O.M., President, in the Chair.

THE following papers were read:—

"The Growth of Seedlings in Wind." By Prof. LEONARD HILL, F.R.S.

Mustard and cress seeds have been grown on lamp wicks in continuous wind of approximately five metres a second, and the central seeds in still air. The seeds grown in the wind are stunted and bent, and contain less water, more ash, less protein, and, presumably, more cellulose.

To counterbalance the drying effect of the wind the seeds have been irrigated with water, and to balance the cooling effect of the wind due to evaporation this water has been warmed, so that a part of the irrigated wick in the wind has been as warm as or warmer than the central wick. By the combining effect of thorough wetting and warming the growth of the seeds in wind has been made much more nearly equal to that of the central.

While the right amount of moisture is the most important factor, the cooling of the germinating seeds by the wind is also a factor in explaining the stunting of growth in wind-swept places.

"The Effect of Thyroid-feeding and of Thyroparathyroidectomy upon the Pituitrin Content of the Posterior Lobe of the Pituitary, the Cerebro-spinal Fluid and Blood." By Prof. P. T. HERRING.

1. Neither thyroid-feeding nor thyroparathyroidectomy in cats affect the pituitrin load of the posterior lobe of the pituitary body as tested by the action of similar strengths of extract upon the rat's uterus, and the blood pressure of the pithed cat.

2. There is no evidence of the presence of pituitrin in the cerebro-spinal fluid of the fourth ventricle in normal, thyroid-fed, and parathyroidectomised cats.

3. The defibrinated blood of normal, thyroid-fed, and thyroparathyroidectomised cats has no appreciable action on the rat's uterus.

The blood of thyroid-fed cats has a greater depressor action upon the circulation of an anaesthetised cat than has the blood of the normal animal.

The blood of thyroparathyroidectomised cats has a pressor effect upon the circulation accompanied by contraction of the kidney and a diminution in the secretion of urine.

"Reflex Times in the South African Clawed Frog." By W. A. JOLLY.

The reflex times of the homonymous and heteronymous reflexes in the hind limbs of the spinal clawed frog have been measured at temperatures ranging from 14° C. to 30° C. The average heteronymous time (66 observations) is 18.7 σ (0.0187 second). The average homonymous (68 observations) is 14.9 σ . That is to say, the crossed reflex time is longer than the same-side reflex time by 3.8 σ .

It is suggested that the experiments can be divided into two classes, the chief determining factor being the general condition or "fitness" of the spinal preparation. In the first class, where the preparation is normal and the temperature fairly high, the average heteronymous time is 15.7 σ and the average homonymous 14.3 σ . Since the difference between the crossed and same-side reflex times is here very brief, viz., 1.4 σ , and as in some experiments the crossed reflex time is the shorter, it is concluded that the intraspinal paths of the two reflexes are similarly constituted as regards number of synapses; that is to say, each path normally involves one synapse.

In the second class, where the frog is not in the best condition, either on account of a recent operation or from long survival since operation, the short path is not open for the crossed reflex, and a longer path containing two additional synapses, or three synapses in all, is employed. The average heteronymous time is here 23.7 σ , and the average homonymous 15.7 σ , giving an excess delay for the crossed reflex of 8 σ .

The delay at a synapse in the spinal cord is found to be about 3.7 σ . This is considered to be referable to a single synapse, but it is not intended to exclude the possibility that it represents the delay at a set of synapses.

"Cellular Immunity. Observations on Natural and Acquired Immunity to Cobra Venom." By Prof. J. A. GUNN and R. ST. A. HEATHCOTE.

(a) *Natural Immunity.*—The minimum lethal dose of cobra venom for the cat is twenty times that for the rabbit (by subcutaneous injection per kilogram). When the excised hearts of rabbits and cats are artificially perfused with Locke's solution so as to remove the serum, it is found that it requires at least four times as strong a solution of venom to arrest the cat's heart as is required to arrest the rabbit's heart. Similarly the isolated intestine of the cat can withstand the toxic action of higher concentration of venom than can the isolated intestine of the rabbit. The natural immunity of the cat to cobra venom is therefore in part at least due to a cellular immunity of the tissues of this animal. No such cellular immunity is displayed by the red blood corpuscles, those of the cat being actually more sensitive than those of the rabbit to the haemolytic action of the venom.

(b) *Acquired Immunity.*—When a rabbit is immunised to cobra venom, the isolated heart and intestine, perfused with Locke's solution so as to remove the serum, withstand higher concentrations of venom than the heart or intestine of a normal unimmunised rabbit. In the process of acquired immunity, therefore, some of the tissues at all events develop a cellular immunity, apart from the antitoxin circulating in the serum.

In the rabbit immunised to cobra venom the red blood corpuscles, freed from serum, become, on the other hand, more sensitive to the haemolytic action of the venom. At the stage of immunity which has been examined, they display no cellular immunity. When a rabbit is immunised to ricin, the red cells also become more sensitive to the agglutinating action of this toxin.

"Studies on Synapsis. III.—The Nuclear Organisation of the Germ Cells in Libellula depressa." By L. T. HOGGEN.

(a) The nuclear organisation of the germ cells in *Libellula depressa* is investigated with a view to further knowledge of: (i.) relation of kinetic processes in premeiotic and meiotic phases; and (ii.) bearing of nuclear emission in oocyte upon integrity of chromosome complex in meiotic phase.

(b) In the premeiotic telophase the chromosomes spin out into finely granular loops, displaying initially a polar disposition, becoming increasingly more attenuated in the spirophase, and first recognisable individually in the prophase as attenuated convoluted filaments.

(c) The Leptotene bouquet is regarded as owing its character to the polarisation of the normal telophase. The failure of modern cytological research to confirm the existence of Flemming's continuous spireme makes it imperative for those who advocate telosynapses in animal forms to postulate some means whereby terminal union can be effected in a manner consonant with observed data, respecting the premeiotic telophase and the initial events of synapsis. Zoological telosynapists have not been able to do so, and the interpretation here presented excludes the possibility of reduction by any means other than lateral approximation.

(d) The behaviour of the "double nucleolus" has been thoroughly studied the plasmosome is independent of the chromatin organisation of the nucleus. It is submitted that the question of nuclear emission, vitellogenesis, and secondary nuclei can now be placed on a basis compatible with integrity of chromosomes throughout the meiotic phase of female germ cells.

INSTITUTION OF MINING AND METALLURGY.

November 18, 1920.

Mr. FRANK MERRICKS, President, in the Chair.

THE following papers were read:—

"An Automatic Counting Machine for Checking Tram Waggons." By CYRIL BRACKENBURY.

At a quarry in which the workmen were paid on piecework, their wages depending chiefly on the number of waggons of material sent to the dump, and over the weighbridge, the author devised a

simple scheme for registering each waggon as it passed up the incline. The up line was provided with catch rails for the purpose of derailing runaway waggons, and, as each waggon passed the open switch the wheel flanges moved the rail. Suitable levers and wires connected the switch with an automatic counting machine situated in the office, with the result that every complete movement of the switch rail registered a new unit on the counter. In this manner both the management and the workmen were satisfied that a correct record of the movements of the tram waggons could be kept.

"Converting High-Grade Matte in Magnesite-lined Converters." By H. C. ROBSON.

This paper contains a record of work done at the Spassky Copper Mine, Siberia, where two 10-foot "Great Falls" magnesite-lined converters were installed in place of three 5-foot acid-lined converters, in 1915. From the start the new converters were run with the idea of keeping a protective coating of magnesite on the brick lining. This was effected by blowing to white metal a 5-ton charge of matte with flux, followed by a similar amount without flux, and $1\frac{1}{4}$ tons of cold matte, the whole being blown to blister-copper. One of the chief difficulties in converting high-grade matte is keeping the tuyeres open, especially with slags high in iron and low in silica. From his experience the author can see no reason why any commercial grade of matte should not be treated if correct working conditions be maintained; with matte assaying between 55 and 60 per cent copper it was not possible to produce a slag containing less than 6 per cent of copper. A blister-copper assaying about 98.8 per cent of copper with a small percentage of sulphur was always produced; attempts to produce copper of a higher grade caused difficulties by the cooling of the charge. The paper contains tables showing respectively the operating data of the converters, analyses of the converter products and by-products and particulars of the operating temperatures in three trial charges.

SOCIETY OF PUBLIC ANALYSTS.

Ordinary Meeting, November 3, 1920.

Mr. ALFRED SMETHAM, President, in the Chair.

The following papers were read:—

"The Gravimetric Estimation of Bismuth as Phosphate and Its Application in Ore Analysis." By W. R. SCHÖLLER, Ph.D., and E. F. WATERHOUSE.

A modification of the method for the gravimetric estimation of bismuth as phosphate is described, the directions being sufficiently explicit to render the method easily applicable even if the operator has only an occasional determination to make. A process for the determination of bismuth in ores is also described in detail; in this the lead is removed by iron wire; copper, arsenic, and antimony by extraction of the sulphides with sodium cyanide and sulphide, and the bismuth converted into and weighed as phosphate.

The authors endorse Moser's opinion of the phosphate method, *i.e.*, that in the great majority

of cases it should prove the most advantageous method, and be accorded first place in the textbooks.

"The Time Factor in Saponification." By PERCIVAL J. FRYER, F.I.C.

Determinations were made of the rate of saponifications under certain specific conditions of temperature, solvent, and concentration of alkali, of various oils belonging to the different classes of oils and fats, with a view to ascertaining if such differences in rate are sufficiently great to form the basis of an analytical method for identifying individual oils and fats.

"Apparatus for Collecting Samples of Water at Great Depths." By W. T. BURGESS, F.I.C.

The device is supported by a single wire, and the sample is collected in a stout glass vacuum tube protected by a cylindrical casing through which the water can pass freely. When at the required depth the upper end of the exhausted tube is broken by the motion of a plunger operated by a falling weight. The apparatus is suitable for taking samples from very deep wells or borings of small diameter.

Ordinary Meeting, December 1, 1920.

A Certificate was read for the first time in favour of Mr. W. R. Schoeller, Ph.D.

Certificates were read for the second time in favour of Messrs. Urban Aspey, Herbert Corner Reynard, B.Sc. (Lond.), A.I.C., Edwin Burnhope Hughes, B.Sc. (Lond.), A.I.C., Harry Jephcott, M.Sc. (Lond.), A.I.C., Arnold Lees, A.I.C.

The following was elected a Member of the Society: Mr. T. K. Chose, B.A., L.M.S. (Cal.).

The PRESIDENT referred to the regret with which the Council had received the resignation of Mr. J. L. Baker from the editorship of *The Analyst*, a position which he had so ably filled for the past 13 years, and congratulated him upon his appointment to the editorship of the *Journal of the Institute of Brewing*. The President announced that the Council had appointed Mr. C. A. Mitchell as his successor.

The following papers were read:—

"Estimation of Theobromine." By RAYMOND V. WADSWORTH.

The author in the present paper criticises the ordinary processes employed for the estimation of theobromine, and suggests a new method based on the employment of calcined magnesia and extraction with tetrachlorethane.

"A New Process for the Estimation of Small Quantities of Chromium in Steels." By B. S. EVANS, M.B.E., M.C., B.Sc., F.I.C.

The process provides a means of estimating quantities of chromium of the order of 0.01 per cent which are outside the scope of the accepted methods. The steel is dissolved in sulphuric acid and oxidised with nitric acid, about 25 grms. of ammonium phosphate added, and the whole boiled with excess of potassium permanganate to convert the chromium into chromate. The acid liquid is poured into excess of boiling caustic soda solution acidified with acetic acid and made up to a known volume; an aliquot part is filtered off, made strongly acid with sulphuric acid, and the

chromium determined colorimetrically by matching with N/100 potassium dichromate. The process has been tested from 0.003 per cent up to 15 per cent of chromium, and gives good results over the whole range.

"Some Notes on the Reactions between Fulminate of Mercury and Sodium Hyposulphite." By P. V. DUPRE, M.B.E., A.C.G.I., F.I.C., and F. H. DUPRE.

The authors describe the titration of fulminate of mercury in sodium hyposulphite. The effect of boracic acid in retarding the secondary reaction causing loss of alkalinity, and the evolution of heat caused by secondary reaction is then discussed, together with the bearing of this on the method of destruction of fulminate by hyposulphite. The effect of boracic acid on heat evolution is dealt with, and the final products in interaction between fulminate and sodium hyposulphite described.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. November 8, 1920.

SPECTRA OF SAMPLES OF MERCURY, COPPER, ZINC, AND THALLIUM IN THE EXTREME ULTRAVIOLET.—MM. Leon and Eugene Bloch.—I. *Mercury*.—The authors have continued Lyman's researches; they have found 36 new rays between 1650 and 1400 U.A., beyond those published by Lyman.

II. *Copper*.—The copper spectrum has been studied by Handke up to 1594.2 U.A. The authors have found that the spectrum seems to end with a group of four characteristic rays situated beyond the limit reached by Handke.

III. *Zinc*.—The zinc spectrum extends much further than copper into the extreme ultraviolet. It has been measured by Saunders up to 1603.09, and by Handke up to 1632.9. Recently, Millikan has extended it almost to 1200 U.A. without giving any exact values. The authors give the results of their measurements between 1850 and 1445 U.A.

IV. *Thallium*.—Up to now no definite record of the thallium spectrum has been made. The authors give a list of the rays between 1850 and 1477.2 U.A.

CORRESPONDENCE.

THEORY OF RELATIVITY.

To the Editor of the Chemical News.

SIR,—A copy of the CHEMICAL NEWS for November 12 has been kindly forwarded to me with a letter by Mr. B. H. Crookes specially marked. Mr. Crookes states that a study of Prof. Einstein's book on "The Special and General Theory of Relativity" has led him to the conclusion that the whole theory of relativity is based on a fundamental error. In addition he considers that the results obtained at the solar eclipse which are taken as verifying Prof. Einstein's predictions are in reality due to distortion of the photographic film. He mentions displacements detected by Sir W. Crookes in spectra and assigned to this cause. Astronomers are alive to the possibility of such displacements. They are of very small amount, and extend over very limited distances. The

possibility of displacements of this character occurring in the eclipse photographs was suggested to me by Prof. Silberstein. I invited him and Dr. Mees, the Director of the Research Laboratory of the Kodak Company, an expert on these questions, to come to Greenwich and inspect the seven photographs taken at the eclipse. Dr. Mees, as soon as he saw the photographs, said that he agreed with us at Greenwich that the displacements of the stars could not be accounted for in this manner. At a meeting of the Royal Astronomical Society a few days later, Prof. Silberstein, in presence of Dr. Mees, stated that he had discussed the point in connection with the eclipse results, and believed the effect to be negligible (*Observatory Magazine*, June, 1920, p. 211). If Mr. Crookes will consult the current number of the *Astrophysical Journal* giving the results of Dr. Ross' experiments made at the Research Laboratory of the Kodak Company he will see how small displacements of this character are, and to what a short distance they reach. After this, a glance at the reproduction of one of the eclipse photographs given in *Phil. Trans.*, A. 220, 291, will show that displacements due to chemical and mechanical causes in the film are negligible.—I am, &c.,

F. W. DYSON.

Royal Observatory, Greenwich.

ENQUIRIES.

To the Editor of the Chemical News.

SIR,—We are advised through an advertisement of the British Association of Trade and Technical Journals that inquiries are invited on commercial and technical questions by the members of the Association.

We are, therefore, asking for the following information relative to one of our products and in connection with our intention to manufacture in Great Britain should conditions be favourable.

1. What is the normal price at which "Rosin" of about "G" grade can be purchased in barrel lots laid down in London?
2. What are normal quotations on Gilders Whiting or what you might term ground chalk?
3. What is the price per cwt. on petrolatum or mineral jelly of $\frac{1}{2}$ grade?

This information will be greatly appreciated, and trusting that we may have a reply as soon as possible—I am, &c.,

F. E. HENEY,

General Manager,
Canadian Auto Accessories Co.

Ottawa, Ont., Canada.

INSTITUTION OF ELECTRICAL ENGINEERS.—The Ordinary Meetings of the Institution during the Session 1920-21 will be held at the Institution of Civil Engineers, Great George Street, Westminster, at 6 p.m.

APPOINTMENT.—Sir John Francis Cleverton Snell, Member of Council of the Institution of Civil Engineers and Past President of the Institution of Electrical Engineers, has been appointed by an Order of Council dated the 23rd day of November, 1920, to be a Member of the Advisory Council to the Committee of the Privy Council for Scientific and Industrial Research.

Blackie's New Books in Science and Philosophy

THE FOUNDATIONS OF CHEMICAL THEORY

An Introductory Textbook. By R. M. CAVEN, D.Sc. (London), F.I.C., Professor of Inorganic and Analytical Chemistry in the Royal Technical College, Glasgow. Royal 8vo. Price 12s. 6d. net.

A concise account is given in this book of the foundations on which the structure of modern chemistry is reared. The story is simply told with the essential technique. The book meets the needs of degree students in chemistry, who require a book introductory to the larger treatises on physical chemistry.

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ELECTRICITY AND ITS PRACTICAL APPLICATIONS

A Textbook of Electrical Engineering. By MAGNUS MACLEAN, D.Sc., Professor of Electrical Engineering, Royal Technical College, Glasgow. Fully illustrated. Demy 8vo, price 12s. 6d.

This book is designed to cover the subjects treated in a first-year course of Electrical Engineering. Special care has been taken to explain clearly the physical facts which underlie the action of all electrical machinery and appliances. Ease in calculating electrical quantities must be acquired by every electrical engineer, no matter what special branch he may take up, and to make the path as easy as possible for the student, a large number of worked examples and exercises, *with answers*, are given, and a special Appendix has been written explaining the Electrical Units employed in Engineering.

APPLIED OPTICS THE COMPUTATION OF OPTICAL SYSTEMS

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METEOROLOGY

An Introductory Textbook. By A. E. M. GEDDES, O.B.E., M.A., D.Sc., Lecturer in Natural Philosophy in the University of Aberdeen. (*Ready Shortly*.)

A concise and clearly written account of the modern science of Meteorology. A knowledge of the elements of the subject is now essential to air pilots, naval and military officers, and navigators; while "the weather" and the "how" and "why" of its vagaries are full of interest to everyone.

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TIDAL LANDS

A STUDY OF SHORE PROBLEMS

By ALFRED E. CAREY, M.Inst.C.E., Fellow of the Royal Geographical, Geological, and Chemical Societies, and F. W. OLIVER, F.R.S., Quain Professor of Botany in University College, London. Copiously illustrated with 29 full-page plates in addition to figures in the text. Demy 8vo. Price 15s. net.

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LIFE AND ITS MAINTENANCE A SYMPOSIUM ON BIOLOGICAL PROBLEMS OF THE DAY

The contributors include: W. M. Bayliss, F. G. Hopkins, E. Margaret Hume, A. R. Cushny, K. J. J. Mackenzie, E. J. Russell, R. G. Stapledon, A. S. Horne, Sydney J. Hickson, A. G. Tansley, Lt.-Col. Martin Flack, R. C. M'Lean, F. W. Oliver, H. M. Vernon, Henry Kenwood. Price 5s. net.

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Latest Patent Applications.

- 34274—Atack, F. W.—Oxidation of hydrocarbons. Dec. 4th.
 34139—Blichfeldt, S. D.—Saccharification of starchy materials. Dec. 2nd.
 34124—Casale, J.—Apparatus for catalytic synthesis of Ammonia. Dec. 2nd.
 33948—Dreyfus, H.—Manufacture of solutions, compositions, and having a basis of cellulose acetate, &c. Dec. 1st.
 33958—Dunningham, A. C.—Manufacture of sodium thio-sulphate. Dec. 1st.
 33848—Farbwerke vorm. Meister, Lucius, & Bruning—Manufacture of derivatives of 3: 3'-diamino-4: 4'-Dioxyarsenobenzene. Nov. 30th.
 34273—Fox, N. T.—Means for concentrating liquids. Dec. 4th.
 33983—Fytelman, M. E.—Separating asphaltum, bitumen, tar, &c. from mineral matter. Dec. 1st.

Specifications Published this Week.

- 154304—British Cellulose & Chemical Manufacturing Co., and Soller M. Hotz, J.—Manufacture of Acetic Acid.
 154300—Nielsen, H., and Marshall, F. D.—Gas-washing apparatus.
 154310—Nielsen, H., and Marshall, F. D.—Air saturating towers.
 154382—Wilton, N.—Manufacture of sulphate of ammonia, and apparatus therefor.
 154368—Matheson, H. W.—Apparatus for the manufacture of acetic acid.
 154472—Napp, H. R.—Manufacture of hydrobromic acid from bromine and hydrogen.

NOTICES.

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3167.

EDITORIAL.

THE Department of Overseas Trade have issued a small booklet in which the vital necessity for the development of our overseas trade is very clearly set out and some sound advice is given which in our opinion should be brought to the notice of all manufacturers. Copies of the handbook may be obtained by United Kingdom merchants and manufacturers on application to the Department of Overseas Trade, 35, Old Queen Street, Westminster, S.W.1, quoting reference No. 2092/TG.

We are pleased to reproduce the introductory chapter by the Right Hon. F. G. KELLAWAY, M.P.

THE NEED FOR GOVERNMENT ASSISTANCE TO COMMERCE.

In looking beyond the immediate present, the most casual observer is forced to the conclusion that the fiercest struggle for foreign trade since our merchant adventurers first set sail will soon engage the whole fabric of British industry. For us, and for most other nations, the only way of replenishing the national coffers, and replacing that vast wealth which has been expended and destroyed, is to increase our overseas trade.

The more quickly we develop our export trade, and so strengthen our exchanges, the sooner we shall lighten the burden of taxation, and this, of necessity, is of great personal interest to each one of us. If we look at the present-day position geographically and commercially, we see how the very existence of this country depends upon its overseas trade.

The United Kingdom is exceptionally dependent upon outside sources for foodstuffs and for raw material for its industries. We must sell extensively abroad in order to be able to purchase our requirements from abroad. In other words, we stand or fall by our export trade.

Before the war, 78 per cent of the wheat and 40 per cent of the meat for home consumption came from overseas. When we take raw materials into consideration as well, we find that nearly 80 per cent of our imports comprised commodities which we must import.

This will give some idea of the extent to which we are dependent upon other countries, and any reduction of our imports through inability to pay by our exports would materially and adversely affect the prosperity of the community as a whole.

Communications and transport are of the first importance to a successful development both of home industry and overseas trade; but of scarcely less importance is the collection and dissemination of commercial information. Every trader will recognise at once the urgent necessity of knowing what his competitors are doing, how matters relating to overseas markets stand, and what are the conditions and prospects in them for our overseas trade. In keeping himself fully posted as to conditions abroad and as to openings for business, the individual initiative of the trader counts before anything else. The Government

can only assist. It cannot be, and does not aim at becoming, more than an accessory. Let us make our minds quite clear on this point. Interest does NOT mean interference.

Since Government interest in commercial matters is recognised and felt to be a national necessity by every other great Power, surely we, in view of our insular position and vital dependence upon outside sources for supplies of food and raw materials, have the greater need for Government assistance. It was expressly with the object of giving this help that the Department of Overseas Trade was instituted in the summer of 1917, and there is already ample evidence that its alliance with British traders has directly contributed to the expansion of British export trade.

The more frequently British traders have recourse to the Department, the more useful it will be.

Any firm in the United Kingdom engaged in the export of British goods can make use of the Department's services free of charge, and no preferential treatment is made by the Department between the large and small firm, between the manufacturer and the merchant.

THE PHYSICS AND CHEMISTRY OF COLLOIDS AND THEIR BEARING ON INDUSTRIAL QUESTIONS.*

SOME PRACTICAL APPLICATIONS OF ELECTRO- ENDOSMOSE AND CATAPHORESIS.

By W. R. ORMANDY, D.Sc., F.I.C., Etc.

THE number of industries which have arisen out of the deliberate application of the theoretical laws relating to electro endosmose and cataphoresis are comparatively few and there is not much progress to record since the issue of the second report on Colloid Chemistry which appeared in 1918.

The work, which has issued from the laboratory of the Elektro Osmose Aktiengesellschaft, still remains the largest contribution to this class of work. Undoubtedly the Schwerin patents applied to the purification of clay form one of the most interesting practical adaptations of the complicated physical laws dealing with colloids.

The history of the development may be described briefly as follows:—

First the discovery that suspensions of many clays could be so treated by a direct current of electricity as to bring about the deposition of the clay in a more or less dry state on a negative pole. It was found that all clays did not react and a second series of patents deal with the possibility of increasing reactivity of the clay particles to the electric current by adding traces of suitable electrolytes which were absorbed by the clay.

Further work showed that even with the addition of suitable electrolytes there were clays which were not amenable to electrical separation or at any rate not in a sufficiently pronounced degree to render the process commercially applicable. A third series of patents was taken out claiming the use of added colloidal substances which would be adsorbed by the clay, which colloidal substances

*A General Discussion before the Faraday Society and the Physical Society of London, 25th October, 1920.

were then capable of adsorbing the necessary electrolytes, and for this purpose such bodies as silicate of soda, humic acid (Casseler brown earth) and the like were employed. Count Schwerin was one of the first to realise the possibility of applying the comparatively new scientific discoveries relating to colloids to industrial purposes. So far as my knowledge goes, he was the first man to recommend the addition of electrolytes, with or without other colloids, to clay suspensions, with the object of converting the clay into the sol condition so that the sedimentation of the heavier impurities might take place. It is impossible by mixing a plastic clay with even a large amount of water to separate the bulk of the impurities without losing a lot of clay substance and without the use of an excessive amount of water. The free silica which is always present in clay is surrounded by clay in the gel form and the separation of this clay from the particle only takes place when suitable electrolytes are added so that the clay is peptised and separated from the silica.

The osmose machine applied to the separation of the suspended particles is an interesting example of the application of comparatively recent physical-chemical laws. In the preparation of the clay we make use of the laws of selective adsorption, of the influence of adsorbed colloids and finally of the directive effect of an electric current on a suspension of particles in the sol condition. On the anode of the osmose machine the negatively charged particles are deposited and the moment a film of these exists over the anode, brought about by cataphoresis, electro endosmose comes into action and the water in and around the clay is electrically driven through the capillary spaces resulting from the close contact of the clay particles deposited on the anode. It is interesting to note that the amount of moisture remaining in the clay attached to the anode is intimately related to the physical nature of the clay substance. If china clay is being worked upon it will be found that if sedimentation is carried out to such extent that only 50 per cent of the clay substance remains in suspension, so that only the finer particles of the clay remain, such a suspension treated on the osmose machine will give a product containing approximately 28/32 per cent of water. If the china clay which has settled out be now remixed with water and passed through the osmose machine—that is, if we make use of the coarser clay particles only—the osmose machine will yield a product containing 35/40 per cent of water. On the other hand, if similar experiments be carried out with a very plastic ball clay having much finer particles in the sol suspension, the osmose machine may deliver a product containing as little as 18 per cent of water. It would appear as though the percentage of water in the clay delivered from the osmose machine were due in some measure to the fineness of the state of division in the sol state and to some extent also it is a measure of the plasticity.

In treating a very pure specimen of a well-washed English china clay by the osmose process, it has been found possible to deposit as much as 6833 kilogrms. of dry clay substance with 11·8 kilowatt hours of current when working at 50 volts pressure.

It is interesting to regard this deposition of clay by direct electric current as though we were dealing with the deposition of copper from a solution

of one of its salts. On the basis of the figures given above, we should have to assume that the equivalent weight of china clay was of the order of 700,000 and that where a given current would deposit 1 grm. of hydrogen or 31½ grms. of copper, it would deposit 700,000 grms. of clay. Needless to remark, these figures can only be obtained when working with very pure clay and with water of very low conductivity.

It has been stated that the electro osmotic process does not bring about any purification of the clay material in the actual osmose machine, but, whatever may be the position theoretically, the fact remains that in practice such a purification is brought about, as has been proved beyond all doubt at the laboratory of the Osmosis Company, Limited, by Mr. Lawrie, when working on tons of china clays and ball clays.

Peat.

The application of the electro-osmose filter press to colloidal peat suspensions results in the removal of large quantities of water at a comparatively low cost in fuel; thus hydraulically mined peat, containing only 5 parts of dry peat substance in 100 parts of suspension, results in the removal of 85 parts of water from the 100 parts of mixture, with an expenditure of current which can be produced by the consumption of one-sixth of the resultant fuel. The ultimate drying of the product from the filter press containing 1 part of peat to 2 parts of water is comparatively simple, but the difficulties attached to the use of the process are more largely mechanical. Unfortunately peat is generally found in comparatively thin layers, and owing to the small percentage of dry substance contained in the peat, the osmose plant would soon be far distant from the point where the fuel was being worked. It is obvious that the process lends itself particularly to application in countries where water-power is available for producing the necessary electricity.

Colloidal Silica.

By passing an electric current through silicate of soda solutions it is possible to drive out the soda and leave the silicic acid behind, but this can only take place if diaphragms are employed which will permit of the soda ions passing out of the silicate of soda solution and will not permit of backwards way diffusion into the inner chamber. Years of experiments have resulted in the development of such diaphragms, and it is now possible to produce silica solutions up to 30 per cent in strength, but the stability of these solutions diminishes as the concentration increases. It is interesting to note that the stability of these silica solutions has been found to increase with each step in progress which has been made, resulting in the more complete removal of the sodium salts. These silicic acid solutions of 5/10 per cent strength have been largely used on the Continent for therapeutical purposes, and the strong solutions after polymerisation result in the formation of a gel, which, on drying, produces an inert highly electro-negative finely divided colloidal gel, which has proved to have extraordinary properties as an adsorbent for use on wounds. In the Third Report on Colloid Chemistry, p. 123, there is a reference to a statement by W. Ostwald "that fresh colloids (particularly silica) will pass through a membrane, but after keeping a few days they will not pass through." It adds, "there is no

connection between the rate of diffusion through the membrane and the molecular weight." It has been found that the silicic acid solution produced by the electro-osmose process, at the moment of its preparation, has a molecular weight corresponding to the formula H_2SiO_3 , and that the molecular weight increases steadily with the time, until a 10 per cent solution, after about 6 weeks, the molecular weight has reached something in the order of 60-80,000, and obvious separation takes place. If a 10 per cent solution of silicic acid be kept in a vessel lined with paraffin wax, it is possible, by means of conductivity experiments, to determine the age of the preparation to within a few hours. It would seem likely, therefore, that the ability of new solutions to diffuse through a diaphragm is directly and closely connected with the molecular weight. No doubt Ostwald's less pure solutions polymerised to such an extent in a few days that they could no longer pass through a diaphragm.

Tanning.

It would appear that a very great simplification has taken place in the plant now used for electric tanning of skins. Two factories in Germany are at present employing the process, and the chief claim made is that it permits of the utilisation of very dilute tanning liquors, with complete utilisation of the tanning material. It is further claimed that experiments have shown that it is preferable to complete the tanning for two or three days in the ordinary way in strong liquors, and that the current consumption is thereby reduced from 20-25 kilowatt hours per square metre of hide; when complete electrical tanning is employed, to 6 or 7 kilowatt hours per square metre; when finishing in strong liquors is employed. Here, again, progress has resulted entirely from the discovery of suitable membranes for the enclosing of the anode and cathode.

Ore Separation.

It has been found that if a finely ground ore be suspended in water, that in many cases it is possible to add traces of electrolyte which are selectively adsorbed. If such finely ground ore be allowed to fall through a column of water to which has been added the necessary quantity of suitable electrolyte, and if a current be passed through the water at right angles to the path of the falling particles, the charged particles are drawn on one side and fall into separate receptacles, bringing about concentration of the ore.

Iron ores occurring in clay deposits have been concentrated by the removal of the clay substance on the lines above described.

Anti-Diphtheritic Serums.

It has been found that the anti-toxin contained in the blood serum of a horse is combined, for the most part, with the para-globulin, very little being combined with eu-globulin, and practically none with the fibrinogen. It has proved possible by using suitable diaphragms to separate from the anti-diphtheritic serum of the horse a pure para-globulin containing the bulk of the anti-toxin previously present in the serum. Such anti-diphtheritic globulin is free from amino acids, and from the decomposition products of the albumen bodies such as albumose and petones, and bodies

containing ferments such as katalase, enzymes, and the like. Furthermore, it is claimed that the anti-diphtheritic product so prepared is free from toxon. It has been urged that anti-diphtheritic serum of a horse may, and probably does, contain toxins which have been combined in a weak way with anti-toxins, and that these compounds may split up in the human body with the setting free of toxins which may lead to, and be the cause of, the dangerous secondary symptoms which so frequently occur after serum injection. It is claimed that the electro-osmose process separates the toxon as such, as well as splitting the compound of toxin and anti-toxin with separation of the toxin. The resulting pure anti-toxin para-globulin has concentration six to ten times that of the best horse serum.

Gelatine.

By the use of diaphragms very similar to those employed for the separation of the constituents in serum, it has proved possible to prepare exceedingly pure gelatins from low grade gelatin, and even from glue. These gelatines are so pure that a 5 per cent solution may be kept for weeks or months without any bacterial growth occurring therein, owing to the fact that the whole of the food material which is necessary for bacterial growth has been so entirely removed. Such gelatine is being prepared in this country, and is being tested for photographic and other purposes.

The Removal of Oil from Water.

The electrical methods which are employed for the removal of oil from watery emulsions is really an application of cataphoresis. The oil globules are charged by adsorption of the inorganic salts present in traces, and pass to the anode.

Dewatering of Oils.—It is well known that many tars produced by distillation and many natural paraffin oils contain water in a state of emulsion which is very difficult to separate. Just as the application of direct current electricity has for some time been employed as above stated for the separation of oil emulsions from water, so similar electrical methods are used for the removal of the water particles forming the disperse phase in oil as a continuous phase. This application is very largely used in the Californian oilfields.

THE PROCESSES OF DESSICATION OF LINSEED OIL.—Two samples of oil, North American and Argentinean, were placed in flat glass capsules, in a compartment protected against dust but not the air for 105 days, stirring twice daily. The following modifications were noted:—

	Before.	After.
American oil density ...	0.9342	0.9717
American iodine index ...	188.4	149.0
Argentinean oil density ...	0.9323	0.9485
Argentinean iodine index ...	173.0	154.9

Subsequent researches confirmed the long-known fact that rapidity of oxidation depends upon thickness of the layer.—*Rev. Chim. Industr.*, July, 1920.

PERIODIC CLASSIFICATION OF THE
ELEMENTS.

By J. R. PARTINGTON.

IN connection with the diagram of the Periodic System due to Mr. Nodder, published in the *CHEMICAL NEWS* of December 3, I may mention that a similar diagram, in which there is only one spiral, will shortly appear in my book on "Inorganic Chemistry," which is to be published by Macmillan. In my diagram the atomic numbers are represented, and the Soddy-Fajans relation is also clearly apparent. The statement of

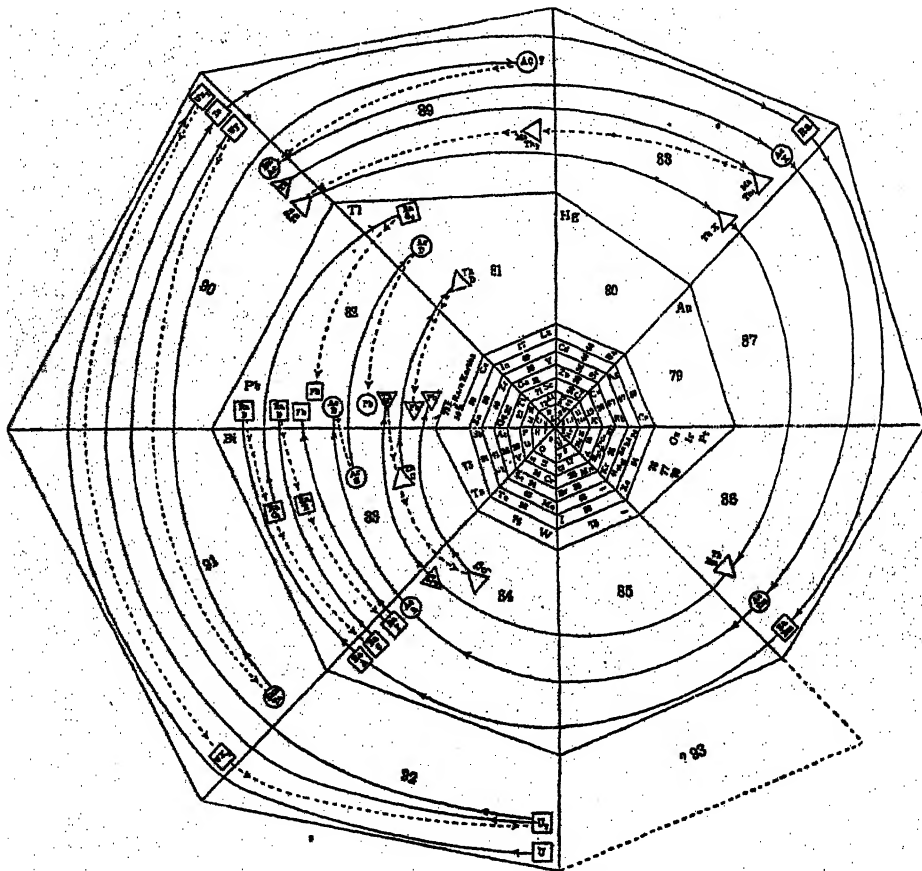
THE ORIGIN OF PRIMARY ORE
DEPOSITS.*

By J. MORROW CAMPBELL.

(Concluded from p. 295.)

THE question as to whether the low-temperature ores when present in a magma with the high-temperature ores pass up the original fissures to higher levels or not is one which is not easily proved, for, in most places, the upper portions of veins which may have contained them have been denuded away.

In the case of some veins in Cornwall we have



PERIODIC ARRANGEMENT OF ELEMENTS.

this principle in connection with the ordinary Periodic Table presents difficulties. For instance, the transitional elements must be omitted, and it is necessary to use two partial tables instead of representing the whole changes in one. I believe that this method of using a spiral, with cells representing the atomic numbers of the elements, has many advantages over that commonly used.

I see no particular advantage in using a double spiral; in fact, many interesting relationships are thereby obscured.

Chemical Department,
East London College (University of London).

proof that copper passed up the fissures in the same solution that carried the tin and was deposited along with tourmaline above the level of the tin.

In Burma and elsewhere we know that reopening of tin and wolfram-bearing veins has resulted in the introduction of copper, zinc, and lead sulphides.

The only reasonable inference, therefore, is that when such ores are present in the magma carrying tin and wolfram they pass up the fissures that

*From *Bulletin of the Institution of Mining and Metallurgy*, October, 1920.

are now occupied by the high-temperature ores. Any other hypothesis would be illogical, and we have good reason for believing it to be the same siliceous medium that carried them all.

Tin and wolfram-bearing veins, however, are not all of this multiple type. Some extend in a single line for many thousands of feet parallel to the axis of the mother batholith. It is evident that there is some difference in the cause of fissuring in the two types.

The writer has ascribed the origin of the multiple type to the percolation of meteoric water down to the magma at these points, and no other explanation so far offered seems capable of accounting for the phenomena displayed by this type.

The long single vein parallel to the axis of the batholith may be accepted as the more normal, for this is what we should expect as the result of ejection of mother-liquor along the ridge of a batholith. Few of these exist in Burma, but they are characterised by having been reopened several times, and contain molybdenite, wolfram, cassiterite, scheelite, bismuthinite, chalcopryrite, pyrites, pyrrhotite, blende, galena, and stibnite, besides mica and fluorite with the high-temperature minerals and quartz which accompanies them all. In one we have "micropegmatitic" growth of quartz in pyrrhotite, which seems to indicate that a pyrrhotite-silicic acid eutectic is capable of existing.

It is believed that much more information of a definite nature concerning the cause of fissuring, as well as the conditions of filling of veins, is to be obtained by patient study of the high-temperature deposits rather than of any others.

The Upward Succession of Ore Minerals.

Lindren classifies primary ores as follows:—

1. High-temperature deposits.
2. Deposits formed at intermediate depths.
3. Deposits formed near the surface.

This classification is a very useful one, but its author probably attaches undue importance to the presence of accessory minerals. As an example chalcopryrite-tourmaline deposits are regarded as high-temperature, whereas chalcopryrite without tourmaline is placed among deposits formed at intermediate depths.

It would be preferable, perhaps, to adopt a classification strictly according to relative temperature of origin without reference to depth, since temperature is of much greater importance in the matter of ore deposition than distance from the surface. In the present state of our knowledge there is nothing definite in either. Both have altered by a varying amount since Silurian or even Tertiary days.

In place of (2) and (3) above, "Intermediate Temperature Deposits" and "Low Temperature Deposits" are suggested.

Consideration of the actual temperature limits of the three classes would be hopeless with the data at present available, and exact knowledge of such, even if attainable, probably would not be of great economic importance.

Regarding the upward succession of ores, lack of space prevents our mentioning any but the most important ones. We shall deal only with ore minerals occurring in veins deposited therein directly by magmatic solutions, and we assume

them to be carried in silicic acid. We also assume that an open fissure exists up which solutions pass. Pneumatolysis, in this connection, is entirely rejected.

At its opening the temperature in the fissure immediately above the batholith is abnormally high, but at no great distance upward it is normal and falls at the normal rate for the district as the surface is approached. After the first inrush, the flow of ore-bearing liquid in the fissure is probably slow, and at all points its temperature is a little higher than that of the walls, heat being transferred from the former to the latter. As the flow is slow and the volume of wall-rock enormous, no very great degree of heating of the latter is possible. The liquid on leaving the batholith carries, say, tin oxide and chalcopryrite in solution, its temperature falls as it passes upward, and at a certain point cassiterite commences to deposit and continues to do so upward until all the tin in solution is exhausted. This will take place when the liquid has fallen to a temperature at which it can no longer hold tin in solution. The temperatures at the two points which are the lower and upper limits of tin deposition give the temperature range of the formation of cassiterite. The same liquid carries chalcopryrite and some iron disulphide as well. Along with cassiterite some pyrites is usually deposited—this mineral is peculiar in the respect that it is deposited in veins at all temperatures—high, intermediate, and low. No chalcopryrite was deposited with the cassiterite below, but near its upper limit chalcopryrite commences to develop and continues until a point is reached where the temperature of the liquid no longer permits it to hold copper in solution. Here again we have a range of temperature within which chalcopryrite deposits; the hotter limit is nearly coincident with the cooler limit for tin, but the two may overlap slightly.

It is evident that the local temperature gradient in the strata is the principal factor in determining the vertical distance in the vein through which any particular ore will be deposited, the lower this gradient the greater the range or persistence in depth.

The average gradient is about 1° C. per 100ft. of depth. Morro Velho gold mine in Brazil provides an extreme example of persistence in depth (over 6,400ft.), and there the temperature increase averages only 1° C. per 140ft. of descent.

The vertical range in veins of such ores as chalcopryrite rarely amounts to as much as 2000ft., and, taking the temperature gradient at normal, this distance represents a temperature range of only 20° C. From this we are forced to conclude that the temperature limits within which any particular ore is developed are very narrow.

It seems likely that there is for each metal a definite maximum and minimum temperature between which its deposition as a primary ore takes place; above the maximum it remains in solution entirely, and below the minimum the primary solvent cannot retain it.

There seems a possibility that this temperature range may be modified to a slight extent (probably varying in the case of each metal) by pressure. Such modification is regarded, however, as not amounting to more than a few degrees of temperature. Since the variation in temperature involved

between the extreme vertical limits of the occurrence of the ores of any particular metal in veins does not appear to amount, even in the case of tin and tungsten, to as much as 100°C. , or in the case of copper to 50°C. (and is probably considerably lower in both cases), it is readily understood that variation in pressure might bring about such varying differences with different metals as to alter materially the paragenetic phenomena in the case of such ores as those of tin and tungsten.

If this principle is true its recognition will simplify greatly the problems presented by the hydro-thermal theory of vein filling.

In the case quoted above where Lindgren classifies chalcopyrite as both a high temperature and intermediate ore, depending whether tourmaline is present with it or not, there appears to be no adequate reason for supposing that the presence of the radicles entering into the composition of tourmaline, when along with those of chalcopyrite in the primary solution, could bring about the deposition of chalcopyrite in a vein at a higher temperature than if no fluorine or boron were present.

Chalcopyrite develops in veins immediately above cassiterite whether accompanied by tourmaline or not, and it must be regarded as developing from magmatic solutions at a lower average temperature than cassiterite.

Deposition of the sulphides of zinc, lead, antimony and mercury, takes place at successively lower temperatures than copper, and therefore they occur at shallower depths as a rule, or at greater distances from the magma from which they emanated. With the possible exception of the last named all the above ores are believed to be transported in silicic acid solution. The case of mercury may be somewhat different, since we know that it is being brought up to the surface in hot springs in several places with sulphuretted hydrogen, alkaline sulphides, and borates. But the same water is highly siliceous in all cases, even where it emerges on the surface, therefore, even in the case of cinnabar, silicic acid may be the carrier, the sulphur being no more necessary for its transport than is the boron which frequently accompanies it.

The temperature range within which gold may be deposited appears to be greater than with many other ores. In many respects it resembles pyrites with which it is so often associated.

It has been noted already that gold is a metal that is being deposited at the surface from solution in thermal waters.

The evidence of hot springs, however, must be accepted only with great caution, because the metals they deposit, the accessory minerals they carry in solution, and the gases they evolve may not be brought up from magmas but dissolved out of deposits traversed on their way to the surface. Even if it were proved that thermal waters carry metals in sulphide solution on emerging on the surface, it does not follow that the metals are of magmatic origin or, if they are, that they left the magma in sulphide solution.

Such waters are usually the meagre residue of mother-liquor given off by magmas now undergoing differentiation that has passed up through

fiissures and deposited the bulk of its load of ore minerals and silica.

We must attach great importance to the fact that so many hot springs are siliceous, and it is somewhat remarkable that no connection seems to have been suggested in the past between them and ore transportation, for they have been regarded commonly as of magmatic origin.

Conclusion.

Magmatic mother-liquor carries silica in solution at all temperatures and pressures, and deposits some of it at every level from the granite to the surface. It also carries various metals in solution, some of which may be deposited at any level from the granite to the surface.

Silica and water are the only invariable products secreted by the mother-liquor throughout the whole of its upward passage, and no other substance is invariably present in it.

Fluorides, borates, sulphides, etc., cannot be regarded as other than accidental constituents, and one or more of them may be deposited in the granite, along with tin or along with copper minerals, gold, or galena, and may even be carried to the surface in solution, but none is invariably present at any particular level.

Surely this demonstrates that these so-called mineralisers do not perform any essential function in ore transportation.

It is illogical to imagine that high-temperature ores are transported in one way in nature and the others in other different ways.

Common sense demands that we should credit the substances essential in magmatic liquid, and invariably present in it, with the principal role in ore transportation, instead of attributing this function to various accidental constituents that are not always present in it.

The theory here advanced is believed to be capable of explaining problems concerning igneous rocks and primary ore deposits where presently accepted theories fail. It is the result of over three years' field work in Burma, first on wolfram and tin, and later on a variety of other ore deposits.

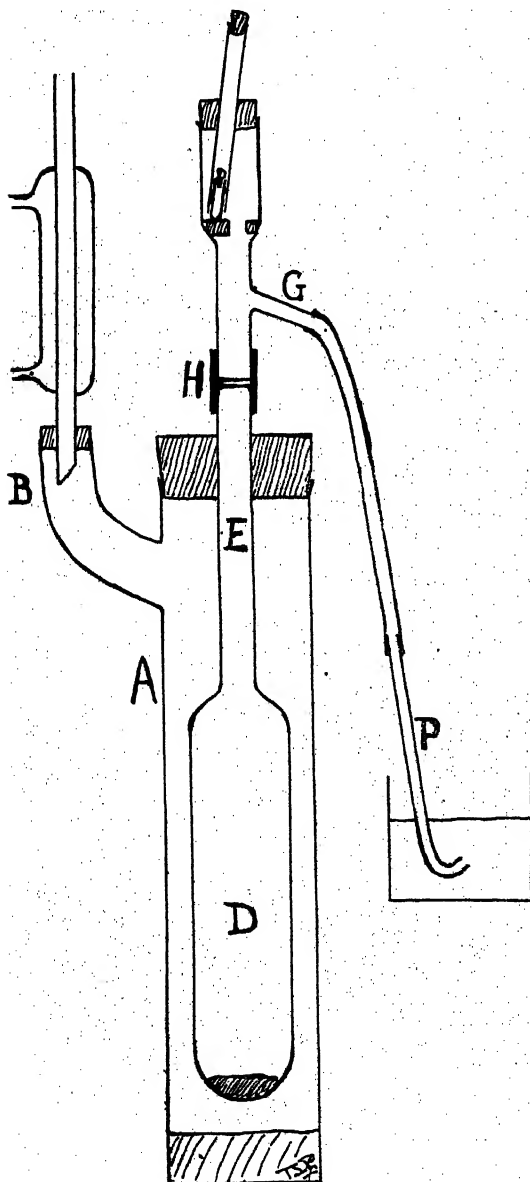
The inadequacy of our present knowledge was felt acutely, and the writer hopes that discussion of the ideas embodied herein may be of assistance to both geologists and mining engineers.

THE NEW NORWEGIAN TITANIUM WHITE INDUSTRY.—Titanium white is much employed for artists' paints and in the porcelain industry. The base of this white is ilmenite, a mineral found only in the Ural and Scandinavia. Owing to the presence of this mineral titanium white is of exceptional interest to Norway. The "Norsk A-S for Elektrokemisk Industri de Fredriksstad" has built a large works for its manufacture. The titanium ore is attacked by sulphuric acid at a high temperature, the iron being then removed by washing. The residue consists of titanic acid, silica, and insoluble gravel. Finally, calcination and washing give the titanium white.—*Rev. Chim. Industr.*, July, 1920.

A SLIGHT MODIFICATION IN VICTOR MEYER'S VAPOUR DENSITY APPARATUS.

By T. S. PATTERSON.

IN view of Mr. A. Price's letter in your issue of November 19 (p. 249), I should like to say that for the past thirteen or fourteen years, I have used copper in place of glass for the outer tube of Victor Meyer's Vapour density Apparatus, with most satisfactory results. The apparatus I use consists of a copper tube, A, closed, by brazing, at the lower end. It has a short side tube, B, brazed on at the upper end, as shown in the accompanying sketch. Into the upright portion of B, a small condenser is fitted.



The ordinary inner tube of the Victor Meyer apparatus is then cut across at H and the tube E is fitted, as shown, to a large rubber stopper. The two parts of the apparatus are then joined together again at H by a piece of fairly thick india-rubber tubing. For the release of the little vessel containing the substance, the arrangement described by me in the CHEMICAL NEWS (1908, xcvi., 73), is used. The side tube, G, is connected by means of a convenient length of narrow rubber tubing to the delivery tube, P. A small quantity of mercury is put into the bulb, D, to break the fall of the little glass tube. The apparatus is heated by boiling any suitable liquid in A. I generally use amyl alcohol. The apparatus thus fitted gives very accurate results.

Organic Chemistry Department,
University of Glasgow.
Nov. 22, 1920.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, December 9, 1920.

PROF. C. S. SHERRINGTON, President, in the Chair.

THE following papers were read :—

"Double Refraction and Crystalline Structure of Silica Glass." By LORD RAYLEIGH, F.R.S.

1. Although glasses in general have no double refraction, except that due to bad annealing, yet silica glass is found to have a doubly refracting structure, which cannot be so accounted for, and must rather be regarded as crystalline.

2. The double refraction is very weak, of the order of $1/60$ that of crystalline quartz.

3. In a mass of silica which has been melted, but not drawn or blown, the structure consists of doubly refracting grains with dimensions of about $\frac{1}{2}$ mm., oriented at random. These grains may correspond to the original fragments of quartz which were melted to form the glass; but this is uncertain. At all events, the grains are very persistent, and individually survive a re-melting of the material.

4. If the grained material is drawn out while soft, the grains are elongated into crystalline fibres or ribbons. These fibres always give "straight extinction" in the polariscope, and their length is along one axis of the *ellipsoid of optical elasticity*, but apparently not always along the same axis. The fact that the crystalline grains can be made to flow in this way assimilates them to Lehmann's *liquid crystals*.

5. If the material is bent or twisted, the fibres follow its course unbroken, and are always extinguished in the polariscope if the nicols are set along the tangent and normal to their direction at any point.

6. Fused silica sometimes contains isolated small inclusions of quartz, with angular outlines, which have escaped vitrification. These are conspicuous in the polariscope by the strain effects they produce in the surrounding glass.

7. Discs of "optical silica," which are built up by a special process, show a most curious strain structure, on which the crystalline grains are superposed.

A heat treatment is described which resulted in the complete disappearance of all this structure and its subsequent reappearance.

"Effect of Asymmetry on Wave-length Determinations." By Prof. J. W. NICHOLSON, F.R.S., and Prof. T. R. MERTON, M.A., D.Sc., F.R.S.

(1) The apparent displacement of an unsymmetrical spectrum line caused by the finite resolving power of the spectroscope can be calculated on certain simple assumptions.

(2) The displacement is independent of the actual widths of the lines.

(3) It is considered that the general practice of measuring spectrum lines to a degree of accuracy far transcending the resolving power is not justified.

"Effect of Concentration on the Spectra of Luminous Gases." By Prof. T. R. MERTON, M.A., D.Sc., F.R.S.

Certain spectroscopic phenomena appear to be associated with the concentration of the radiating atoms in the source. An increase in concentration may result in a broadening of the lines, a change in the structure of the lines, and changes in the relative intensities. Sources containing lithium exhibit these three phenomena, and the broadening is familiar in sodium flames. A study has been made of the behaviour of sources containing sodium and lithium. The results seem to exclude a temporary association of atoms as the cause of the changes, for the addition of large quantities of sodium to a source containing a trace of lithium produces no change in the lithium spectrum. Mixtures of hydrogen and helium have also been investigated.

The broadened lines of both these elements from vacuum tubes excited by condensed discharges are accounted for completely by the electrical resolution of the lines by the electric fields of neighbouring charged particles. Although the broadening of lines of the diffuse series of helium is less than that of the Balmer lines of hydrogen of equal term number, the helium line $\lambda=4471$ Å. is found to be very broad, whilst the hydrogen line $H\delta$ is sharp when the proportion of hydrogen present is very small. With an increased proportion of hydrogen the Balmer lines begin to broaden. It would appear that the electric resolution due to the proximity of a charged particle to the radiating atom depends on the nature of the charged particle, and that the mutual influence of charged atoms of the same kind on one another is vastly greater than that of different kinds of charged atoms.

Phenomena have been observed which suggest that when condensed discharges pass through vacuum tubes containing mixtures of hydrogen and helium, a partial separation of the gases is effected, the hydrogen being selectively driven out of the capillary into the bulbs of the vacuum tube.

"Measurement of Low Magnetic Susceptibility by an Instrument of a New Type." By Prof. E. WILSON, M.Inst.C.E., M.Inst.E.E.

The paper deals with the design, construction, and working of an instrument for the measurement of susceptibility (of low order) over a wide range of magnetic force, and thus avoids the difficulty met with in the Curie balance, the defections of which follow the square law, and, in fact, limit

the measurement of susceptibility of a given specimen to a very narrow range of magnetic force. The force due to torsion in a suspending fibre is replaced by an electro-magnetic system in which the mechanical force is due to two components—one proportional to the magnetic force impressed upon the specimen and the other variable if the susceptibility varies. The expression for the susceptibility is that of the reciprocal of a resistance multiplied by a constant, and thus the instrument lends itself to a great accuracy in the detection of variations in susceptibility.

"The Internal Energy of Inflammable Mixtures of Coal-gas and Air after Explosion." By Prof. W. T. DAVID, M.A., D.Sc.

In the first part of this paper an empirical law of cooling of exploded mixtures of coal-gas and air contained in a closed vessel has been formulated. This is based upon measurements of the heat loss by conduction and by radiation made during the explosion and subsequent cooling of the inflammable mixtures.

In the second part the heat loss measurements have been applied to the estimation of the internal energy of the gaseous mixtures at the moment of maximum temperature and at various stages during cooling. Curves connecting the internal energy and gas temperature have been prepared for mixtures of various strengths. An examination of these curves indicates that the internal energy during the early stages of cooling is a function of the time after explosion, as well as of the temperature of the gas. The interpretation of this is that combustion is not complete at the moment of maximum temperature and continues during the early stages of cooling. It is estimated that only about 90 per cent of the heat of combustion is transformed into thermal energy by the time the maximum pressure is reached, and that combustion is proceeding for at least 0.25 seconds after this moment.

The factors limiting the pressures developed are discussed and a quantitative estimate made of their relative importance in mixtures of various strengths.

"Multenions and Differential Invariants." By Prof. A. MCAULAY.

The paper is a summary of the properties of a linear associative algebra suitable for electro-magnetic relations, differential invariants, and relativity. There are n fundamental units, otherwise it is the same algebra as that considered in a paper by W. J. Johnston and read to the Royal Society on November 20, 1919.

THE FARADAY SOCIETY AND THE INSTITUTE OF METALS. (SHEFFIELD SECTION).

At a joint meeting of the Faraday Society and the Sheffield Section of the Institute of Physics held on Friday, November 19th, 1920, in the Mappin Hall of the Department of Applied Science of the University of Sheffield, a series of Papers on "Electro-deposition and Electroplating" were presented and discussed.

The afternoon session, which was presided over by Prof. C. H. DESCH, D.Sc., was devoted to problems relating to Electro-deposition generally.

"Electroplating for the Prevention of Corrosion." By Dr. LESLIE AITCHISON (communicated by W. R. BARCLAY).

The paper dealt more especially with the protection of iron and steel and their alloys. The conditions for proper protective coatings, namely, permanence and resistance and non-permeability to corrosive agents, were defined and the value of the various protective coatings discussed with relation thereto. In particular, the relative advantages of hot coating and cold electro-deposition were considered and the general advantage of zinc deposition over galvanising was emphasised.

The properties required in a metallic protective coating were classified as follows:—

1. Uniformity.
2. Permanence.
3. Good appearance.
4. Freedom from porosity.
5. Freedom from pinholes.
6. Good adhesion to base metal.
7. Reasonable ductility.
8. Freedom from scaling or flaking.
9. Penetration into all parts of a complicated surface.
10. Minimum tendency to promote corrosion of the base metal if the coating is pierced.

Special emphasis was laid on the need for ductility and condition 10 was discussed and some apparent anomalies set forth. Finally the preparation of the surface was dealt with.

"Some Applications of Electro-Deposition in Aeronautical Engineering." By W. A. THAIN, A.M.I.C.E.

Three cases of the electro-deposition of copper were considered, viz.: (i.) as a protection against carburisation in case-hardening practice; (ii.) as a means of increasing heat conductivity; (iii.) as a means of building up a definite constructional detail.

As an example of (i.) the treatment of a camshaft was considered. In case (ii.) copper-plating of the steel cylinder of an aeronautical engine was examined. The deposit is of the order of 0.003-inch thick, being greatest at the top of the flues and least at the foot. Finally an account was given of the details in the building up of the copper-water jacket of a Beardmore aero-engine cylinder. The final thickness of the jacket wall is 1.7 mm.; it is tested under water pressure of 25-30 lbs. per sq. inch, and as hundreds of such cylinders had stood the test of active service, the method had been thoroughly proved and must be considered a sound practical proposition.

"The Electro-deposition of Cobalt." By BYRON CARR.

From a bath containing 4½ lbs. of cobalt sulphate crystals, 5½ ozs. boric acid, and 2½ ozs. of sodium chloride per gallon and used at 34° C., excellent hard adherent deposits of cobalt were obtained, provided that these were not too thick, with 150 and 72 amperes per square foot respectively. Periods of immersion not exceeding 2 and 4 minutes respectively were suitable. The deposit is exceedingly resistant to atmospheric corrosion and is superior to nickel in the rapidity of deposition and hardness. Articles of domestic use so

treated were, however, subject to the deleterious action of fruit juice.

"The Use of Colloids in the Electro-deposition of Metals." By W. E. HUGHES, B.A.

Colloids and substances producing the same effects were often usefully employed in electroplating solutions. In one case at least—that of lead—no coherent deposit could be obtained unless some colloid, for instance, glue or peptone, was used. The effect usually produced by the colloid addition was a diminution of the size of grain of which the deposit consists, the diminution being, in some cases, so extreme that, to the naked eye, the deposit appears plastic and non-crystalline. The mechanism of the change from macro-crystalline to micro-crystalline was unknown. The differing views of Marc, Kohlschütter, and Freundlich and Fischer were referred to, and it was suggested that this difference of opinion was in itself sufficient reason for drawing attention to the operation of colloids in plating solutions, which was of interest both practically and theoretically.

"The Commercial Electrolysis of Zinc Sulphate Solutions." By S. FIELD, A.R.C.Sc.

The electrolysis of zinc sulphate solutions is carried on commercially in cold galvanising with a zinc anode, and in the electrolytic recovery of zinc, using an insoluble lead anode. In the latter case the solution contains a percentage of acid prior to electrolysis, and this increases as the zinc is deposited, usually on aluminium cathodes. A neutral sulphate solution containing 10 per cent of zinc may be produced by leaching ores or other zinc-bearing materials with sulphuric acid or acid zinc sulphate liquors from the electrolytic cells, and this composition may conveniently be altered to 8 per cent zinc and 3 per cent acid before electrolysis. Commercial electrolysis aims at the maximum extraction of zinc from such a liquor with a minimum of energy. The greater the extraction of zinc, the smaller the volume of liquor which circulates through the whole of the extraction plant, and the smaller the proportion of zinc which demands repeated purification. A limit to this extraction is set by the cost of increased energy necessary to take out zinc from dilute liquors, due mainly to a considerable falling off in the current efficiency. Current efficiency is dependent upon a number of factors including current density, amount of zinc present, temperature, and last, but by no means least, the presence of impurities.

Several impurities normally occurring in these crude zinc sulphate liquors exert a marked deleterious effect on the deposition of the metal from these acid solutions. The effect of, among others, nickel and cobalt has been carefully studied. The presence of a few parts of either of these metals per million parts of liquor disastrously lowers current efficiency and increases energy consumption. Traces of cobalt produce an extraordinarily honey-combed deposit, while even smaller amounts of nickel produce large and clean-cut holes in the deposited metal. The types of corrosion exhibit a marked contrast.

Traces of these impurities thus seriously militate against successful deposition. Neither impurity is deposited with the metal but remains in the solution and, concentrating during the cycle of operations, soon places the operation outside

the sphere of economy. Colloids have an ameliorating effect, but of a temporary character only. The elimination of these impurities is an essential to successful deposition.

It is suggested that as the beneficial effects of traces of colloids are known and applied there is justification for keeping a close watch on all impurities in electro-depositing solutions even though the normal conditions of deposition may widely differ.

The evening session was presided over by Mr. E. A. SMITH. The Papers presented all dealt with various aspects of the electroplating of silver.

"Electro-Silver Plating and its Technical Development." By W. R. BARCLAY, O.B.E., A.M.I.E.E.

This paper dealt with the history of technical investigation, and research into the electro-deposition of silver, so far as the more practical aspect of electroplating is concerned.

The work of early authorities, such as Smee, Gore, Langbein, and others, was briefly outlined, but it was pointed out that the main advances belonged to the last twenty-five years, and followed on the work of the physical chemists of the latter part of the nineteenth century, who laid the foundations of modern electro-chemistry.

The investigations of such research workers as Brunner, Foerster, Bancroft, Frary, and Porter, and others, on the influence of current density, metal and free cyanide concentration, and other cognate factors, on the character of silver deposits was discussed, and an outline given of the author's own experience in workshop practice.

Emphasis was laid on the necessity for careful co-ordination of the factors of metal and free cyanide content to that of current density. It was shown that though considerable latitude is allowable in practice, the best results and highest efficiency lie within fairly well-defined limits. With a current density of 2.75 to 3 amperes per square foot (for example) a solution containing 3 troy oz. per gallon with not less than twice a molecular equivalent of free cyanide, gave excellent results as to both quality of deposit, efficiency, and time occupied.

Among other matters it was pointed out that silver solutions in existence over sixty years still continued to yield excellent results, and that generally old solutions yielded better deposits at higher current densities than those newly made up from pure materials. Recent investigations had shown that this was due, in a great measure, to the presence of substances other than the simple double cyanide of silver and potassium, especially potassium carbonate, which salt is usually to be found in a higher proportion than any other, and increases the conductivity to a considerable degree.

While the technical efficiency of a modern silver-plating plant was fairly high, further investigation was necessary as to the exact influence of substances such as potassium chloride, sulphate, cyanate, and formate, all of which had been shown to be present in commercial plating baths, and necessarily made the chemical and electro-chemical reactions of these baths somewhat complex. A question of further importance remaining to be solved was the influence of organic matter on the physical structure of deposits.

"The Chemical Composition of Old Silver-Plating Solutions, with Observations on their Working Properties." By G. B. BROOK, F.I.C., and L. W. HOLMES.

The paper dealt with a large number of solutions varying in age from one to fifty years, furnishing historical, chemical, and physical data with regard to each, and correlating the composition with the working properties in actual works practice. The graph showing the intimate relation of the carbonate content to the electrical conductivity was the outstanding feature of the paper, and constituted in itself a valuable discovery, which promised to have a far-reaching effect on the composition of the plating solution of the future. The comparison of solutions, used respectively by "trade" platers and private manufacturers' plating departments, was of considerable interest.

"A New Maximum Current Density in Commercial Silver-plating." By FRANK MASON, A.M.I.E.E.

During extensive researches on the physical structures of electro-silver deposits, which are at present being carried out at the University of Sheffield, the author observed that in certain instances exceedingly fine deposits of silver were obtained at an extraordinarily rapid rate.

None of the mechanical devices usually associated with rapid deposition are as yet available for production on a commercial scale of thick deposits of silver with a crystalline structure easy to "finish."

Microscopic examination of such silver structures show that these ideal conditions for a high finish are to a large extent governed by the size and position of the crystals of the deposit. Under normal conditions of commercial electroplating the higher the current density used, the larger is the crystal obtained, until the crystalline structure is such that "finishing" is impossible, and the deposit is said to be "burnt." The limiting current density permissible is 3 to 4 amperes per square foot.

During the investigation already referred to the electrolytes from which abnormal silver deposits were obtained always contained potassium carbonate. The metal from these was precipitated in a fine reguline condition, until the percentage of the latter compound reached the neighbourhood of 10 per cent, and the current conditions were normal. Any further increase produced large crystalline structures, very difficult to burnish or polish, and a cathode current density of 6 amperes per square foot brought down a deposit from which the desired final "finish" could not satisfactorily be produced. The solutions containing a higher percentage of potassium cyanide in conjunction with potassium carbonate, somewhat counteracted this undesired effect. It was further found that with a free cyanide content in excess of that usually advised in any up-to-date text-book, and with potassium carbonate in considerable quantities, not only could the current density be increased enormously, but that the deposit was of a finer texture altogether. Sufficient evidence was obtained that the potassium carbonate does really assist in the conductance of the current in an electrolyte of the double cyanide of silver and potassium.

The author has had the process installed on a commercial scale with most satisfactory results,

both as to rate of deposition and character of deposit. After depositing upwards of 8000 ozs. of silver, an analysis of the electrolyte gave the following result:—

Silver	26.14	grms. per litre.
Free potassium cyanide	47.25	" "
Potassium carbonate	165.00	" "

A photomicrograph of a deposit from this bath made with a current density as high as 8 amperes per square foot showed the same structure as a deposition obtained under commercial conditions with a current density of $3\frac{1}{4}$ amperes per square foot.

The reduction of time in deposition, resulting in double the output, should be of considerable value, and the enormous saving in capital outlay in materials and plant will be appreciated by electroplate manufacturers.

"The Crystalline Structure of Electro-deposited Silver. By G. B. BROOK, F.I.C.

The author shows that the normal relatively smooth "reguline" deposit develops, with high current density, a growth of individual acicular crystals from the face of the deposit. In the subsequent burnishing and polishing such structure results in the retention in the interstices of the imperfectly laid-down crystals of the polishing material. It was the investigation of this latter trouble, which had become serious and general in the silver trade, that the author found that very high current density contributed to the particular form of crystal growth (or its free development) and accounted for the retention of the rouge in the final process of polishing.

"The Deposition of Gold-Silver Alloys." By S. FIELD, A.R.C.Sc.

A series of experiments has been carried out in order to trace the influence of varying conditions on the composition of the gold-silver alloys deposited in the well-known "green gold." In cyanide solutions gold is the more positive metal. In the absence of hydrogen deposition, the composition of the deposited alloy can be calculated from the ratio of its mass to that of copper deposited in a coulomb-meter in the circuit. In gilding solutions of normal strengths this ideally quantitative deposition is not attained. The deposits are produced on lead foil cathodes, and, after weighing, are cupelled with added silver to give a "parting" mixture from which the content of gold is determined. Platinum anodes provide the means of most constant control over the composition of the bath, additions of standard solutions of gold and silver cyanides being made after each deposit.

A cold solution containing 14.2 grms. gold and 7.2 grms. silver per litre and without free cyanide was first employed. Increased current density increased the proportion of gold in the alloy. A similar increase occurs in a warm solution but the whole of the gold values are lower than in cold solutions. Diluting the solution also increases the proportion of gold and addition of free cyanide has the same effect, the proportion of gold to silver becoming more constant and independent of other conditions with larger proportions of free cyanide.

By way of comparison, deposits were prepared in a works under normal working conditions. These included a more dilute solution with a

larger gold-silver ratio and a larger proportion of free cyanide. Over a range of current density of one to five an almost constant percentage of 77 to 78 per cent of gold in the deposit was obtained.

NOTES.

LINSEED OIL SUBSTITUTES.—Different combinations of Guiana wood oil, fish oil, and soja oil have been utilised with variable success (W. Buccblans, *Seifenseider Zeitung*, 1920, 2, xlvii., 141). A method of manufacture consists in heating a fine quality fish oil for 2 hours at 240°C ., then distilling with steam at 375° to 400°C . during 30 hours. Thus, a thick elastic material is obtained which has very good siccativ properties. Another method is to heat the oil with 15 per cent water and 0.5 per cent sulphate of manganese in an autoclave during 3 to 5 hours at a pressure of 10 atmospheres. The conclusion arrived at, according to Bruckhams (*Seifenseider Zeitung*, 1920, xlvii., 141) is that practically it is impossible to find a substitute for linseed oil, especially in manufacture of lakes. The mixed varnishes are made with boiled soja, sunflower, and linseed oils. If one wishes to give siccativ properties to non-siccatives such as fish oils, it suffices to mix a drop of glacial acetic acid with them in the tared tube of a centrifugal machine; then all is cooled at -10° to 0°C ., and 1 to 1.2 cubic cm. of bromine added drop by drop. The mixture is left in the refrigerator for 2 hours, and then worked in the centrifugal apparatus. The ether is decanted and the residue recovered in the tube with 2 cubic cm. of cooled ether and again passed through the centrifugal apparatus. The operation is repeated, the precipitate dried at 110°C ., and weighed. The percentages of hexabromides obtained with different linseed oils may vary to 8 per cent. This is why Bruckhams prefers this method to that of Steel and Washburn, which gives 3 per cent smaller results, but usually constant even for different oils.—*Rev. Chim. Industr.*, September, 1920.

ROYAL INSTITUTION.—The following are the Lecture arrangements at the Royal Institution, before Easter: Prof. J. Arthur Thomson, a course of lectures on the "Haunts of Life," adapted to a juvenile auditory, to begin on December 30; Sir Gerald P. Lenox-Conyngham, two lectures on the "Progress of Geodesy in India"; Sir James G. Frazer, three lectures on "Roman Life (Time of Pliny the Younger)," "London Life (Time of Addison)," "Rural English Life (Time of Cowper)"; Dr. Arthur Keith, four lectures on "Darwin's Theory of Man's Origin"; Dr. W. A. Herdman, three lectures on "Oceanography"; Mr. Frank Balfour Browne, two lectures on "Mason Bees and Wasps"; Dr. George C. Simpson, two lectures on the "Meteorology of the Antarctic"; Dr. Percy C. Buck, three lectures on the "Madrigal," with musical illustrations by the English Musical Singers; Prof. A. Fowler, three lectures on "Spectroscopy"; and Sir Ernest Rutherford, three lectures on "Electricity and Matter." The Friday evening meetings will commence on Jan. 21, when Sir James Dewar will deliver a discourse

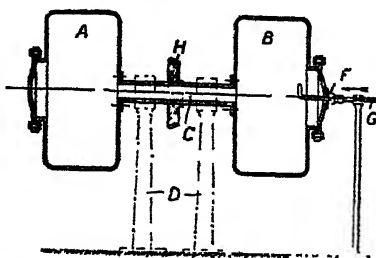
on "Cloudland Studies." Succeeding discourses will probably be given by Sir Frank Benson, Dr. A. D. Waller, Dr. F. W. Aston, Mr. Solomon J. Solomon, Dr. John Buchan, Sir Frederick Bridge, and other gentlemen.

CHRISTMAS LECTURES AT ROYAL INSTITUTION.—Prof. J. Arthur Thomson will deliver the first of his series of Lectures on "The Haunts of Life" at the Royal Institution on Thursday, December 30, at 3 p.m.



This List is specially compiled for *Chemical News* by Messrs. Rayner & Co., of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

Mercuric Oxide.—Mr. C. Brusa and Messrs. Borelli & Co., of Turin, Italy, have recently obtained a patent in this country for means for obtaining mercuric oxide No. 15091. The apparatus for which, is illustrated in the appended drawings. Mercuric oxide is obtained by decomposing mercurous nitrate by heat in a closed chamber; the nitrogen oxides evolved are brought into contact with mercury in presence of oxygen to yield more mercurous nitrate for use in the process. The apparatus shown consists of two revolving bull-mills, A, B, connected by a hollow trunnion, C; a charge of mercurous nitrate is placed in the mill A, and mercury in the mill B, which latter is provided with an oxygen inlet-pipe, G; the mill A is heated and the mill B cooled, so that nitrogen oxides are evolved from the former, leaving mercuric oxide, and pass through the shaft C into B, where they react with mercury and oxygen to reform mercurous nitrate.



[Messrs. Rayner & Co., will obtain printed copies of the published specifications and forward on post free for the official price of 1/- each.

Latest Patent Applications.

- 34683—Baird & Tatlock—Set of cards for teaching chemical formula and equations. Dec. 8th.
- 34715—Bergdahl, B.—Method to produce Ammonia. Dec. 8th.
- 34745—Bird, F. C. J.—Antiseptic and protective coating for the skin. Dec. 8th.
- 34582—Casale, L.—Production of nitrogen or mixtures of nitrogen and hydrogen. Dec. 7th.
- 35014—Scheibler, H.—Process for manufacture of sulphur preparations of the thiophene series. Dec. 11th.

Specifications Published this Week.

- 154680—Dreyfus, H.—Manufacture of Acetic Acid.
- 154718—Mackay, R. A.—Treatment of sulphide ores containing lead and zinc.
- 154910—Datta, R. L.—Manufacture of potassium bichromate and of sodium bichromate and the production of normal sulphates of potassium and sodium.

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THE CHEMICAL NEWS.

VOL. CXXI., No. 3168.

THE PHYSICS AND CHEMISTRY OF COLLOIDS AND THEIR BEARING ON INDUSTRIAL QUESTIONS.

NITROCELLULOSE.*

By SIR R. ROBERTSON, K.B.E., F.R.S.

Introduction.

THE principal applications of nitrocellulose in industry are to celluloid, propellants, artificial silk, colloidion, and some blasting explosives. In this paper I shall confine myself for the most part to nitrocellulose as used in the manufacture of propellants, and I propose to describe some of the relations that exist between the solutions of cellulose and of nitrocellulose and the gelatinised nitrocellulose after the solvent has been eliminated, together with some work on the characteristics of its solutions.

Most of the modern propellants are colloidal in character, and it is to the nitrocellulose which they contain that this character is to be attributed. As they have no definite crystalline structure, and can be obtained as uniform non-porous masses by the process of incorporation or malaxation during manufacture, they present an unbroken surface to the flame which ignites them, and even under pressure continue to burn regularly from layer to layer. It is this property that has enabled guns to be designed much lighter in weight than for gunpowder, and that has made it possible by suitable choice of thickness of the propellant to secure very high velocities of projectiles (within a narrow margin of a few feet per second from round to round) without undue strain on the gun.

To obtain the degree of regularity in ballistics necessary for accurate shooting it is important for the dimensions of the finished propellant to be within very narrow limits. It has been found that the nature of the nitrocellulose used affects the amount of shrinkage which takes place in the cord after squirting from the die, and it is obvious therefore that the colloidal properties of nitrocellulose gelatinised by means of solvents, either volatile or non-volatile, are of great importance in the study of propellants.

I propose to bring to your attention the results of some work on gelatinised nitrocellulose that has been carried out at the Royal Gunpowder Factory, and the Research Department, Woolwich.

Among the more important aspects that have to be considered are the influence on the product of the nature of the raw material, the influence of the process which it undergoes in being nitrated and stabilised by boiling with water, and the effect of these on the characteristics of the finished material. Among other important properties the viscosity of solutions of cellulose and of nitrocellulose in relation to these aspects clearly required investigation.

Treatments which affect the Viscosity of Cellulose and Nitrocellulose Solutions.

In general, those treatments which would be expected to affect disruption of molecular aggregates (e.g., by grinding or chemical decomposition such as hydrolysis) are found to lower the viscosity both of cellulose and nitrocellulose solutions.

The treatment of the cellulose before solution, with bleaching powder (oxidation) or caustic soda (hydrolysis) in the usual processes of cleaning, reduces the viscosity of its solution in cuprammonium. The viscosity of the solution itself is reduced by exposure to air or light, or even to some extent by simply allowing it to stand for some time. The viscosity of the solution of the corresponding nitrocellulose is found to be affected in the same direction.

With the nitrocellulose, the steam boiling treatments given in the purification process lower its viscosity, but there appears to be a practical limit to the process. When the more easily attacked forms of nitrocellulose have all been destroyed by boiling, the further reduction in viscosity is very slow, and if the cellulose before nitration has been treated so as to reduce its viscosity markedly, no great reduction of viscosity is produced by boiling the nitrocellulose.

In order to produce a nitrocellulose of low viscosity, it is found to be better to reduce the viscosity of the cellulose as far as possible by suitable treatments than to rely on the reduction during boiling of the nitrated product.

It may be mentioned parenthetically on the question of the measurement of the state of molecular aggregation of nitrocellulose in solution, that in a recent paper by Duclaux and Wollman (*Bull. Soc. Chim.*, xxvii., 420), emanating from the Pasteur Institute, while the lower limits of molecular weight of nitrocellulose solutions are shown by measurements of osmotic pressure to be very high, the molecular weight of products of different degrees of viscosity varied from aggregates of 80 times the C_e formula for cellulose to 270 times in the case of the more viscous samples.

Relation of Viscosity of Solution and of its Nature to the Toughness of the Dried Nitrocellulose Colloid.

In some earlier work the viscosity was measured by means of a viscosimeter of a simple type, and the toughness of the resulting gelatinised dried nitrocellulose in the form of cord was evaluated by determining the least radius of curvature to which the cord could be bent. This method brought out such differences as that a cord of nitrocellulose of 13 per cent nitrogen content cracked at a radius of curvature of 100 millimetres when acetone had been the solvent, while a cord of nitrocellulose of 12.4 per cent of nitrogen broke at a radius of 25 mm. again with acetone as the solvent, and at 5 mm. when ether-alcohol had been used to gelatinise it.

From the results of these experiments it was deduced that when the same simple solvent (acetone) was used to gelatinise nitrocelluloses of a high nitrogen content (13 per cent) the viscosity of the nitrocellulose solution was inversely proportional to the toughness of the resulting cord. The coherence of the dried nitrocellulose was thus found to be adversely affected by the higher state of aggregation of the molecules of the nitrocellulose, as indicated by the viscosity of its solution.

*A General Discussion before the Faraday Society and the Physical Society of London, October 25th, 1920.

This short note on these experiments has been given, as they illustrate a connection between the viscosity of a solution and the physical consistency of the dried nitrocellulose.

The nature of the volatile solvent also affects the brittleness of the dried gelatinised substance. Thus the dried product made by gelatinising nitrocellulose of 12.4 per cent nitrogen with ether-alcohol is much tougher than that gelatinised with acetone, and a similar effect is obtained by adding some alcohol to the solvent acetone. Caution has, however, to be observed in this connection, as retention of the solvent in an imperfectly dried substance may give a quite fictitious semblance of toughness to a film of gelatinised nitrocellulose. Thus when films of nitrocellulose of 13 per cent nitrogen are made with acetone and with amyl acetate respectively, clear acetone films of about 0.5 mm. in thickness (and these can be made by taking precautions to prevent access of water vapour during evaporation of the solvent) seem to be much more brittle than similar films made with amyl acetate. When, however, the latter are dried out so that all the solvent, in this case of considerably higher boiling point than acetone, is eliminated, the film is quite as brittle as that in which acetone is the solvent.

Processes for Determining the Viscosity of Cellulose and of Nitrocellulose Solutions.

It might now be well to refer to some of the methods that have more recently been found most suitable for determining the viscosity of solutions of cellulose and nitrocellulose, and to state briefly the information that study of this property has afforded. Of great importance in this connection has been the application of the Falling Sphere Viscosimeter (Gibson and Jacobs, *J. Chem. Soc.*, 1920, cxvii., 472) in which the velocity is observed of a steel ball, 0.15 cm. in diameter, under standardised conditions, falling through the solution, appropriate corrections being made for deviations from Stokes' law on account of the side-effect of the walls and the end-effect of the bottom of the viscosimeter tube. This instrument has had a wide application in the study of solutions of nitrocellulose, and the difficulties inherent in its application to solutions of cellulose in cuprammonium solution, chiefly on account of the need for eliminating air in this estimation, have been overcome (Gibson, Spencer, and McCall, *J. Chem. Soc.*, 1920, cxvii., 484).

For cellulose dissolved in cuprammonium solution a capillary viscosimeter in which the solution comes into contact only with hydrogen was developed, and the conditions were obtained for the preparation of the cuprammonium solution by a process which gave more reliable results than those described by Ost. By the use of this capillary viscosimeter it is possible to obtain viscosities of more mobile solutions of cellulose in cuprammonium solution than with the Falling Sphere Viscosimeter, for example, below 10 C.G.S. units.

Relation between Viscosity of Nitrocellulose Solution and Cohesion of Dried Nitrocellulose Mixtures.

Reference has been made to a case in which the brittleness of dried gelatinised nitrocellulose was affected by the nature of the original nitrocellulose and associated with high viscosity of the nitrocellulose solution. A similar relationship

came to light when a new nitrocellulose-nitroglycerine propellant (R.D.B. Cordite) requiring ether-alcohol as a solvent was used in quantity during the war, in place of cordite M.D. for which the supply of acetone was insufficient. It was found on pressing the incorporated gelatinised material that the extruded cord exhibited a lack of cohesion and uniformity of diameter which gave rise to difficulties. An investigation of the nitrocellulose and of the cellulose from which it was made was carried out by the application of the processes mentioned above, and ultimately the cellulose was controlled by the Falling Sphere Viscosimeter. By this means the uniformity of the cellulose was ensured, and a limit imposed on its viscosity. It appeared that the lack of uniformity of the pressed cords of this propellant in this case also was due to an unduly high viscosity of the nitrocellulose, and when measures were taken to control the viscosity of the cellulose itself, no further trouble was experienced.

From a consideration of these two examples, one of gelatinised nitrocellulose and the other of a nitrocellulose-nitroglycerin mixture, it would appear that a high state of aggregation of the molecules of nitrocellulose is not conducive to the toughness that is desirable in a product that has to be handled both during manufacture and after.

The subject of the viscosity of cellulose and of solutions of cellulose was further pursued at the Research Department, Woolwich, by the application of the methods of determining viscosity mentioned above, and some of the results obtained in these investigations may now be considered.

Viscosity of Cellulose Solutions and their Relation to Nitrocellulose Solutions.

In the first place, as regards the cellulose itself, the reduction in its viscosity brought about by increase in temperature of the alkaline pressure boiling to which the cotton is subjected, and the influence of increase in the concentration of the caustic alkali in this process in the same direction have been described by Gibson (*loc. cit.*, 481).

Correlations were then made between the viscosity of the cellulose in cuprammonium solution and that of the solution in ether-alcohol of the nitrocellulose made from it, and it was established that although the processes of nitration and stabilising by boiling of the nitrocellulose tended to level down differences, yet there is a general relationship in the sense of higher viscosity of the nitrocellulose made from cellulose of high viscosity, and it was brought out that if the cotton had been incompletely reduced in viscosity by the soda boiling the viscosity of the finally purified nitrocellulose was with greater difficulty brought down by the steaming during stabilisation.

Minimum Viscosity of Nitrocellulose Solutions.

The viscosity of solutions of nitrocellulose in ether-alcohol was then studied (Gibson and McCall, *J. Soc. Chem. Ind.*, 1920, xxxix., 172, T), by the method of the Falling Sphere Viscosimeter, and a suspicion that a small change in the proportion of ether to alcohol affected the viscosity, led to a thorough examination of this variant with ether-alcohol solutions of nitrocellulose of different contents of nitrogen and in different concentrations. It was established that there was a minimum viscosity at a certain proportion of ether to

alcohol, solutions on either side of the minimum being the more viscous, and indeed formed jellies with the higher proportions of either alcohol or ether. The position of this minimum was also found to be independent of concentration, leading to the deduction that this minimum would give the optimum proportions for the solvent used in the process of gelatinisation in the incorporator where the ratio of solvent to substance is necessarily very much less than is any solution of which the viscosity can be measured by the means spoken of above. It may be said that this was verified in practice.

This position of minimum viscosity was found to vary with nitrogen content among those nitrocelluloses which are soluble in ether-alcohol more ether being required for those with the higher content of nitrogen, and it was also established that the farther the composition of the solution is removed from the point of minimum viscosity, the longer does it take for equilibrium to set in, the process of gelation continuing in some of the mixtures rich in one constituent for a considerable time. It proved to be of importance from a manufacturing point of view to choose the mixture of minimum viscosity, since with the associated proportion of ether to alcohol on the one hand, gelatinisation proceeds with the greatest rapidity, and on the other hand, as this mixture has the maximum fluidity, with the smallest usage of solvent. The practical application of this principle in supply, the large scale experimental work carried out in this connection and the means taken to secure that a nitrocellulose of easy gelatinising properties was obtained by the controlled treatment of the cotton itself are described by Mr. R. A. Punter.

The alcohol used in the above work was of 92 per cent strength, and it has been found possible by determining the viscosity of a series of binary mixtures of nitrocellulose in ether and alcohol containing varying proportions of water, to obtain a ternary diagram from which the mixture of ether, alcohol, and water that gives the optimum value of viscosity can be read off.

A similar point of minimum viscosity has been found with acetone-water solutions of nitrocelluloses, and it is of interest that the proportion of water in the acetone thus indicated is one which has long been used in the manufacture, having been chosen from other considerations. The phenomena of the gelation of such mixtures are discussed by Masson (*J. Chem. Soc.*, 1920, cxvii., 819). The relation between viscosity and concentration, as is also the case with ether-alcohol solutions, appears to conform to the Arrhenius logarithmic expression, but only over a limited range.

Concluding Remarks.

The above work has afforded a great deal of information on the nature of the solution of cellulose and of nitrocellulose and forms the basis for theoretical speculation apart from the bearing it has had on manufacture.

The viscosity of the solutions has been proved to have a direct relation to the properties of the dried colloid from which the solvents have been eliminated by drying. The dried colloid, however, presents difficulties in assessing its physical properties. One method of determining its toughness has been mentioned, and determinations of

hardness by the Brinell method, of breaking strain, or of resistance to crushing have been applied, but not so far with much that is informative. One method may be mentioned by means of which variations in the viscosity of the hard colloid may be traced. If large cords be pressed from different composition of the cordite type in which the proportion of guncotton to nitroglycerine is varied, these cords retain a small proportion of the volatile solvent. If now the quantity of this solvent be determined in different concentric zones it is found that as the nitrocellulose becomes dominant, a proportion is reached when the distribution of the volatile matter is no longer uniform but increases regularly from skin to core, the ratio of the content of volatile matter in the different regions remaining constant although the total quantity is reduced in the process of drying. This resistance to the migration of the solvent is some measure of the viscosity of the horny substance, and its regional determination might, perhaps, assist in the investigation of the physical condition of other hard colloids.

It is hoped that the above will show the importance of the application of the investigation of the colloid solutions of nitrocellulose and indicate, perhaps, points of theoretical interest that remain to be followed up.

IS H COMPOSED OF A WHOLE-NUMBER PART (A) PLUS AN AUXILIARY PART (B) AND A ROTATING ELECTRON (C)?

By F. H. LORING.

READERS of the *CHEMICAL NEWS* will remember Masson's discussion in these columns (1896, lxxiii., 283) of the position of hydrogen in the Periodic Table. A further discussion will be found in Friend's "Text-book of Inorganic Chemistry," I., 274. Turning now to the Lewis-Langmuir "Octet Theory" (*Journ. Am. Chem. Soc.*, 1919, xli., particular p. 874), it will be seen that H and He are placed respectively over lithium and beryllium in the table shown. If the table is expanded horizontally by removing the following elements (Table I) from their present sandwiched-in positions and arranging them, as here shown, it brings into prominence the fact that the lower parts of Groups I. and VII. are deficient in members; but of course, elements may be discovered eventually which will fill the gaps.

If it be assumed that hydrogen belongs to Group VII. (Masson) and that it also belongs to Group I. (see Friend *loc. cit.*) the above deficiency is partly made up at the top of the table. It is not necessary for helium to be placed above beryllium, since the former finds its normal place on the extreme left of the table next to Li. The argument thus far is not convincing as the absence of elements in one part of the table may have nothing to do with a relative excess at another corresponding part, though shortage of material may apparently be the cause.

Now referring to Aston's researches, which have pretty well demonstrated that all the elements except hydrogen have whole-number atomic weights, it is evident that the electric

Langmuir has suggested (p. 872) the existence of cells independent of the electrons in them.

Whatever extensions may be possible, the hypothesis would help to account for ordinary hydrogen *not* polymerising to form elements; but without the attendant atom (*b*) it might be so extremely active* that its polymerides would be extraordinarily stable, and thus answer to the known elements.

Other points of interest are: (1) whether the *b*-atom is a nucleus, or (2) whether it is a satellite like the moon; and (3) whether this sub-atom is associated with other elements in such small quantities as not to introduce appreciable fractions in the whole-number atomic weights. The mass of the moon relative to that of the earth is roughly the same as the relative masses of *b* and *a*, but this observation can in no way be significant.

Experimental possibilities suggest themselves.

Continuing the argument, it will be seen that the parts *a* and *b* may be placed in the Periodic Table. Selecting a table which is perhaps of the greatest interest at the present time, the one due to Langmuir (*loc. cit.*), a modified representation (Table II.) is here given. See also Table III.

It will be seen that it is only a short step from *b* to *a* very much as in the two positions of neon, yet these entities occupy extreme places in the Table, and therefore they should have a strong affinity for each other as in the case of F and Na.

The gaps in the Table are just those which seem most difficult to fill. The writer has on one or two occasions adduced arguments to the effect that these gaps may be natural ones notwithstanding the atomic-number sequence. However this may be, the shortage-of-material idea would probably meet both cases.

The character of a compound is determined by the joint character of its component atoms, but if one of these atoms could be reduced, say, in size, one would expect the larger portion to retain its original properties more and more as its associate grows smaller; but for the smaller atom to have negligible influence it must be relatively very small, unless it has a very intense electric field round it as in the case of the electron. In this case, "size" becomes an electrical property and this has to be kept in mind.

In the periodic grouping, some elements such as He, Ne, Ar, &c., resemble one another so closely that one would say that such elements could not carry a small auxiliary part of appreciable magnitude in differential amounts. There are, however, other elements which show such marked changes, for example, chlorine and manganese, that one would expect a conditioning part of appreciable magnitude to be held by the atoms of one of these elements. If now hydrogen is complex, in that it has an auxiliary part *b*, there is no reason why other atoms may not contain the same fractional entity, but which may not be in multiples of any magnitude since their atomic weights are practically whole numbers.

The rare-earth elements still remain partly a mystery, although Langmuir claims that the

"Octet Theory" accounts for them. If the rare earths were not known, or if no elements were known beyond cerium, would the theory have predicted them? In one sense it would, because in this theory each shell must contain cells of equal volume, and as the atom gets bigger there must be more outer cells if the equality is maintained. Langmuir gives the following Table:—

TABLE III.

Shell.	Radius.	<i>n</i>	Axially placed.	In zones.
I.	1	1	1	0
II.	2	4	0	4
III.	3	9	1	8
IV.	4	16	0	16

n=number of cells in one of the hemispheres of the shell. The last two columns give the number of cells and their disposition. See Table II.

Consequently, there is what appears to be an over-crowding between cerium and tantalum and again an overcrowding in the next row between uranium and the emanations, and continuing back to thallium the same state of affairs exists between this element and the emanations. The parallelism is far from perfect as in the case of the radioactive elements the increase is of an isotopic nature; but on the whole it is satisfactory as one might expect certain difficulties to be removed when more details of the atomic design are known. Upon introducing an auxiliary part which conditions the atom the peculiarities of the Table seem to be about what one might expect, while the large fractional part of the atomic weights is due to isotopes.

According to these arguments one can imagine the following causes, so to speak, at work.

1. The cells in the outer shell (see Lewis-Langmuir theory).
2. The electrons in the said cells (see Lewis-Langmuir theory).
3. The number of filled and unfilled cells (see Lewis-Langmuir theory).
4. The presence in certain cases of a fractional entity (*b*).
5. The presence of isotopes.
6. The total number of electrons in the atom.
7. The total number of positive charges in the atom.
8. The mass of the atom.
9. The atomic number.

Assuming now that there are about 8 variables, it is not surprising that the elements should have the known physical and chemical properties in such manifold variation.

Summary.

Hydrogen appears to be unique in not being a whole-number atom. The fractional part of its mass is relatively great. Hydrogen does not find a proper place at the heads of Groups I. and VII. Its chemical activity is evidently such as not to enable it to form stable polymerides answering to known elements. There is a gap at the end of Group I. that does not accommodate any radioactive element. Similarly, there are gaps below manganese which seem difficult to fill, and one of these would have to be filled by a radio-active element which seems improbable. On the hypothesis that all elements are polymerides of hydrogen, a difficulty arises owing to the fractional value, suggesting that the fundamental unit has a mass of 1 exactly. Considering hydrogen as a

*This word is not very satisfactory as it lacks definition, but this may be said of many words used. Similarly, by way of example, the word size applied to atoms may convey quite a wrong idea. In the latter case probably a field of force is involved which by itself is rather indefinite. The radius of a given atom in mass formation with others is quite a definite figure however. There is danger in pressing ideas of these kinds too far one way or the other.

complex atom composed of mass parts $a=1.0000$, $b=0.0077$, and c (an electron) $=0.00055$, a and b could possibly be more properly placed at the heads of Groups I. and VII. respectively, and thus account for the very strong affinity between these parts, and thereby explain the stability of the hydrogen complex (ab), whilst the respective parts alone might have very great affinity, especially a which could polymerise and form the whole-number elements as revealed by Aston's recent experiments. Moreover, constructing a modified Langmuir Periodic Table, the absence of elements in Groups I. and VII. would suggest a shortage of elementary material, so to speak; but this shortage would be made up at the heads of these groups by introducing the entities a and b at these places. This procedure reveals a numerical regularity. The complexity of hydrogen thus indicated would account for the fact that it is not fully eligible for a position at the head of either of the above-mentioned groups. The question of atomic numbers to be assigned to these hypothetical parts is discussed. It is also suggested that such a fractional entity as b might be attached to other elements in small multiples and thus help to account for certain chemical irregularities in the Periodic Table. The fact that ordinary hydrogen is not known to polymerise to form the elements would be expected if it carries an auxiliary part which deprives it of this property.

STAINLESS STEEL.

By J. H. G. MONYPENNY.

THE commercial utilisation of the non-corrodible properties of steel containing about 12 per cent of chromium may be regarded as one of the outstanding events in the metallurgical world during the past decade. Steel, the most widely-used metal, unfortunately corrodes rather easily, and great precautions have to be taken to protect it, especially in exposed positions. This is particularly noticeable in such large engineering structures as the great railway bridges over the Forth and Tay, where painting is going on practically continuously. The production of a type of steel possessing great resistance to corrosion has obviously a great future, and one may safely say that, as yet, only the fringe of the possibilities has been touched.

Stainless* steel contains essentially 11 to 14 per cent of chromium and, for most purposes, not more than about 0.45 per cent of carbon. It frequently contains small amounts of nickel, say up to 1 per cent, but this element has no beneficial effect on the non-corrodible properties, whilst its presence, if unsuspected, may cause trouble in the heat treatment of the steel, since it has quite a considerable effect on the position of the critical ranges of the steel.

From a microscopic point of view, high-chromium steels, such as stainless, have a great deal of interest. Chromium has the effect of lowering the eutectoid composition in steel to a considerable extent. Whereas in ordinary steel about 0.9 per cent carbon is required to produce a structure consisting entirely of pearlite, with 12

per cent chromium, the same effect is produced with approximately 0.3 per cent carbon. Free carbide or cementite appears when the carbon exceeds this amount. In these steels, also, only part of the carbide forming the pearlite goes into solution at the lower critical temperature change on heating (Ac_1), the rest dissolving progressively over a range of some 200°.

The state of combination of the sulphur in these steels requires further investigation. This element is only evolved to a very small extent as sulphuretted hydrogen on dissolving the steel in acids. The evolution method cannot be applied for its estimation, neither can one obtain an ordinary sulphur print on bromide paper. For example, a steel containing 0.07 per cent sulphur only gave a very faint print even after 15 minutes' contact with bromide paper soaked in 10 per cent hydrochloric acid or 15 per cent sulphuric acid. The print obtained was different in type from an ordinary sulphur print in that the impression did not consist of a series of dots but rather of a uniform stain. Evidently the sulphur does not exist as separate particles of either iron or manganese sulphide disseminated through the mass of the steel; apparently it exists in solid solution.

Thermally, the effect of the chromium is to raise the temperature at which the critical ranges occur. The Ac_1 point occurs in the range 800°–830° C., and on cooling sufficiently slowly to prevent any hardening effects, the critical temperature change on cooling (Ar_1) is found at about 750° C.

Stainless steel possesses notable air-hardening properties. A sample one inch or so in diameter, if allowed to cool freely in the air from 900° C., will have a Brinell hardness number of the order of 500. The capacity of the steel to harden increases with the temperature to which it is heated. In other words, the speed of cooling necessary to harden the steel becomes slower as the temperature to which it is heated rises (providing the latter is, of course, above the carbon change-point); also, slower rates of cooling are necessary to soften or anneal the steel when cooled from progressively higher temperatures.

The property of air-hardening is very useful in a steel. Apart from the obvious fact that less drastic methods of quenching are required (with the attendant lessened danger of cracks, warping, or other undesirable attributes of water-quenching), the slower rate of cooling necessary to harden the steel permits samples of large section to be hardened throughout. It also lessens the danger of soft spots due to retarded quenching. Anyone who has had experience in producing a glass-hard surface over a considerable area in an article made of ordinary carbon steel will appreciate the meaning of the last sentence. Owing to its air-hardening properties, however, the steel requires care during the course of manufacture. Billets, bars, forgings, or stampings are usually heated to at least 1000° C. before any operations are carried out, and if the material after being worked is allowed to cool down on the shop floor it will, when cold, be in the hardened condition and will be quite as liable to crack if rapidly or unevenly heated again as any hardened piece of tool steel. Being hard, it will require softening before any chipping, filing, or machining can be done. These troubles, however, may be avoided by allowing

*[The word "stainless" has been retained because it is in general use; "unstainable" is, of course, the correct term.—ED.]

the forged, rolled, or stamped article to cool slowly over the range 800°—600° C. in order that the carbon change may take place and the steel thus becomes soft.

Stainless steels which contain more carbon than that indicated above, if quenched or air-cooled from high temperatures, are comparatively soft to the Brinell test owing to the production of austenite. Such steels, though soft, are un-machinable, the material becoming hard when stressed. Austenitic samples also harden when tempered at about 600° C.; for instance, an actual sample had a Brinell hardness number of 270 when water-quenched, and one of 444 after being tempered at 600° C. Such hardening after tempering has been noticed by several cutlery manufacturers who have, by accident or otherwise, hardened their knife blades from too high a temperature. Such a practice, however, is not to be recommended, as a coarse grain is thereby produced in the blade.

Stainless steel is tempered in the same way as ordinary steel, but higher temperatures are required. A corresponding series of temper colours are formed at the higher temperatures necessary to soften the steel. For example, the following colours were obtained, at the temperatures indicated, on a hardened sample of the steel:—

Straw	300° C.
Brown	400° C.
Reddish purple	500° C.
Light blue	600° C.
Bluish violet	650° C.
Greyish violet	700° C.
Grey	750° C.

Stainless steel has its maximum resistance to corrosion when in the hardened condition. It is then practically unaffected by exposure to moist air, fresh or salt water, or to such organic acids as occur in fruits. Samples buried in soil for three months have retained their original polish, and others have been immersed in vinegar or salt water for days without showing the slightest signs of attack. Tempering the hardened sample up to about 500° C. does not affect its resistance appreciably. Such tempering has also little effect on its hardness. Tempering at higher temperatures lowers the resistance to corrosion, but even in the soft condition the metal is only slowly attacked. Such soft material, for example, is stained by vinegar, but a sample weighing 60 grms. only lost 0.04 g. after three weeks' immersion. A sample of nickel-chrome steel hardened and tempered so as to give the same tensile strength lost during the same time 25 times as much.

Nitric acid, strong or weak, does not dissolve stainless steel either in the hard or soft condition, nor is the steel attacked by concentrated or dilute solutions of ammonia, nor in a moist atmosphere containing ammonia fumes. Sulphuric and hydrochloric acids attack it readily; a 10 per cent solution of the latter in alcohol forms a convenient etching reagent for microscopic work. Dilute solutions of sulphuric acid, at ordinary temperatures, attack stainless steel considerably faster than ordinary mild steel.

The opinion has been held that the non-corrosible properties of stainless steel are only obtained when it is highly polished and that they are then confined to the surface. This is not correct. It is well known that metals in general

have an increased tendency to corrode after they have been cold-worked. Stainless steel is no exception. Turnings of this steel are in a highly distorted condition and hence will rust. Similarly, the surface of a bar from which heavy cuts have been taken is distorted and is more likely to rust than one from which a fine finishing cut has been taken. A ground or polished surface will be still more immune. That polish, however, is not essential is shown by the resistance to corrosion of a fractured surface which has been obtained without distortion.

In addition to its resistance to corroding influences, stainless steel does not scale to any extent when heated at any temperature up to 800°—850° C. A sample heated for seven days in the range 700°—825° C. lost 0.7 per cent of its weight, whereas a piece of ordinary steel heated with it lost 17 per cent.

The suitability of any new type of steel for use in engineering work of any description is largely judged by its behaviour under mechanical tests. A short description of the results of such tests on stainless steel will be of interest. After oil- or air-hardening from a temperature of 900° C., followed preferably by slight tempering at 200°—400° C., stainless steel has mechanical properties comparable with those of the well-known "100-ton" air-hardening nickel-chrome steel. When tempered in the range 650°—750° C., it gives tests highly suitable for many engineering purposes. The values obtained depend on the composition of the steel, but in general are in the following ranges:—

Yield point	30—55 tons per sq. inch
Maximum stress	45—65 tons per sq. inch
Elongation	15—28 per cent
Reduction of area	35—65 per cent
Izod impact	25—70 foot-lb.

Tempering in this range of temperature (650°—750° C.) is also interesting commercially in that the hardness, and therefore the tensile strength only falls very slightly as the temperature increases. When a number of articles has to be tempered to produce a given tensile strength, quite a wide range tempering temperature is permissible—obviously a desirable thing commercially. On the other hand the hardness falls very rapidly in the range 550°—650° C., and the difficulties of tempering in this range are correspondingly great.

During the war the great bulk of the stainless steel produced was used for aeroplane valves. Its value for this purpose lay, apart from its non-scaling property, in its superior strength at a red heat. The exhaust valves, especially of some of the large aero engines, frequently reach a temperature of 750° or 800° C., or even higher, and it is necessary that the valve should have sufficient strength at such a temperature to secure that the stem does not elongate during running. Actual tests obtained on testing mild steel and stainless steel at high temperatures gave the following figures:—

Tensile strength at	Mild steel.	Stainless steel.
600° C.	11.84	24.24
700° C.	6.8	12.08
800° C.	5.04	6.64
850° C.	4.12	6.64

By increasing the carbon content of stainless steel, still higher values may be obtained, e.g.,

15—17 tons at 700° C. and 7·5—8·5 tons at 800° C.

The development of the uses of stainless steel was very largely held up during the war, since practically the whole of the steel made was used for war purposes. It may be confidently expected, however, that the near future will bring about a very noticeable development in the number and variety of its applications. It will also be found that stainless steel is not one steel but a group of steels. Just as in the far-off days "steel" was regarded as a hard product of iron, and little or no attempt was made to grade it into harder or softer varieties, so at present stainless steel is to most people a product having only one distinct set of properties, many regarding it solely as a special type of cutlery steel. In times gone by, as the use of steel became more general, it was realised that by varying the content of carbon or manganese, steels of widely different intrinsic hardness could be produced, and for each purpose some definite "temper" of steel was best suited. In the same way, as the use of stainless steel becomes more general, it will be found that products of different intrinsic hardness (corresponding to the varieties of ordinary steel) can be produced, all of them having the distinguishing property of great resistance to corrosion, but varying among themselves as soft or mild steel differs from file steel. For each use of stainless steel there will be an optimum "temper."—*Journal of the Society of Chemical Industry*, Nov. 30, 1920.

BRACKEN RHIZOMES AND THEIR FOOD VALUE.

By Prof. JAMES HENDRICK, B.Sc., F.I.C., University of Aberdeen.

DURING 1917 and early 1918, when the food position in this country gave cause for anxiety, and when there seemed little prospect of an early victorious end to the war, it was important to investigate all possible sources from which food for human beings or for stock could be produced without putting any further strain on our shipping. Among other things, the rhizomes or underground stems of bracken seemed to offer possibilities which were worth investigation, and consequently an inquiry into their composition and food value and the methods of harvesting and preparing them for use was begun early in 1918, under the auspices of the Ministry of Food. Although the special circumstances which led to this inquiry have now, happily, passed away, it is worth placing on record the results of the inquiry so far as it went.

Bracken is found in great abundance in woodlands and rough lands in Scotland, and in many places it has overrun good pastures. It is said that bracken areas have greatly increased during the past forty or fifty years, especially in those districts where cattle have been replaced by sheep, and that large areas which were once good pasture have in consequence been ruined or, at any rate, much deteriorated. It does not seem to be possible to obtain any statistics as to the extent to which this has taken place.

The damage caused by the spread of bracken on hill grazings was so great that in 1903 the Society offered premiums for machines or implements for

cutting or destroying bracken. A considerable amount of investigation into methods of eradicating bracken has taken place in recent years ("Bracken (*Pteris aquilina*), Life History and Eradication," by G. P. Gordon, B.Sc. *Transactions*, 1916, p. 92). These investigations have almost entirely dealt with the frond or above-ground part of the bracken, which begins to grow about April or May, reaches its full luxuriance in July, and dies down again about October.

Some attempts have also been made to utilise the fronds as food for stock, especially when they are young. On the other hand there is some evidence that they are poisonous when partaken in quantity by animals, particularly when they are fully grown, and the poisoning which thus arises is known as bracken poisoning ("Bracken Poisoning in Cattle in Great Britain," by Sir Stewart Stockman, *Jour. of Comp. Pathology and Therapeutics*, xxx., Part iv., 1917).

The ash of the fronds has been found to be particularly rich in potash, and proposals have been made during the war to combine eradication of bracken with production of potash manure by cutting down the fronds and burning them, and using the ash as a manure on account of its high content of potash ("A Report on the Results of Experiments on Bracken Utilisation and Eradication," by R. A. Berry, F.I.C., *Bulletin* No. 80, West of Scotland Agricultural College).

The frond of bracken springs from an underground stem or rhizome which is commonly known as "bracken root." This consists of strong dark-coloured rods, which are found a few inches below the surface of the soil and vary in thickness from that of a lead pencil to that of an adult finger. They are many feet in length and branching, and in land well stocked with bracken form an interlacing mat of rods three to six inches below the surface.

These rhizomes or root-stocks have been used as food for pigs and other stock in various parts of the world, and even as food for human beings. During the war, reports were received that with food scarcity in other countries, including enemy countries, their value as food was again being tested. It seemed fitting, therefore, that some investigation of their food value should be made in Scotland, in which bracken occurs to so great an extent, and in which expense was being incurred to eradicate it as a pest.

A number of experiments were made to determine the crop of rhizomes which could be obtained per acre, and this was found to be surprisingly large on land well-stocked with bracken. It varies greatly with the conditions and, as might be expected, is greatest on good deep soil, on which the fronds grow to great size and very thickly. On such a soil the crop in one case, in which the produce from 200 square yards was weighed, was found to be over 53 tons per acre in the unwashed state, or 43 tons per acre of clean rhizomes washed free from earth and dirt. In this case the fronds covered the ground so thickly that they smothered out nearly all other vegetation. In other cases, where the bracken was not growing so thickly or so strongly, crops at the rate of 25, 16, and 13 tons per acre of washed rhizomes were obtained. It is evident, therefore, that heavy crops of this material are to be obtained from land which is thickly covered with bracken.

TABLE I.—Composition of Bracken Rhizomes.

Locality.	Braemar, Creag à Bhuilg.						Potatoes.		
	Mugdock Wood, Milingavie, Glasgow	Pitmedden, Aberdeen- shire	1200 Ft.	1800 Ft.	1500 Ft.	Average. 6 Samples	Average of 136 American Samples	Arran Chief Average of 52 Samples	
Date gathered	8/5/18	23/5/18	11/7/18	8/8/18	8/8/18	13/8/18			
<i>Composition of Original—</i>									
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Moisture	79.59	77.53	71.00	69.98	75.43	69.79	73.89	78.3	76.7
Ether extract (oil, &c.)	.25	.07	.59	.26	.25	.39	.30	0.1	—
*Albuminoids	1.39	1.24	2.12	.85	1.15	.75	1.25	2.2	2.2
Soluble carbohydrates	12.02	13.10	14.15	19.95	15.48	20.26	15.82	18.0	—
Fibre	4.54	6.35	7.84	6.87	5.88	6.67	6.36	0.4	—
†Ash	2.21	1.71	4.30	2.09	1.81	2.14	2.38	1.0	—
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	—
*containing total nitro- gen	.22	.19	.34	.13	.18	.12	.20	.35	.35
containing pro- tein nitrogen	.21	.19	.29	.13	.18	.12	.19	—	—
†containing siliceous matter (sand, &c.)	.82	.55	3.40	.74	.56	.67	1.12	—	—
<i>Composition of Dry Matter—</i>									
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Ether extract (oil, &c.)	1.22	.31	2.03	.85	1.01	1.20	1.12	.5	—
*Albuminoids	6.81	5.51	7.32	2.83	4.68	2.48	4.94	10.1	9.4
Soluble carbohydrates	58.91	58.30	48.78	66.68	63.42	67.08	60.53	83.0	—
Fibre	22.24	28.25	27.05	22.68	23.52	22.07	24.30	1.8	—
†Ash	10.82	7.63	14.82	6.96	7.37	7.08	9.11	4.6	—
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	—
*containing total nitro- gen	1.09	.88	1.17	.44	.73	.39	.78	1.6	1.5
containing protein nitrogen	1.06	.88	1.00	.44	.73	.39	.75	—	—
†containing siliceous matter	4.04	2.46	11.71	2.46	2.28	2.21	4.19	—	—

Most of the land which is overgrown with bracken is either rough and stony hill or woodland. In some cases, however, bracken is to be found on good and comparatively level land on which horses and implements could be worked. In such cases it should not be difficult or expensive to harvest the crop of rhizomes. On the other hand, in woodland the trees and their roots seriously interfere with this operation and make it so difficult as to be practically impossible. On rough stony land the difficulty varies according to the nature of the land. On most rough hillsides the crop could only be harvested by laborious hand labour, which would probably render it too expensive to be of any practical use.

In the experiments which I carried out in order to determine the weight of crop per acre, and to obtain a supply of the rhizomes for feeding trials, hand labour was employed. It was found that if the land was cut into squares with spades and turned over, the rhizomes which were thus cut into short lengths, could be easily shaken out with graips and separated quite satisfactorily from the soil and other foreign matters. Although I had no opportunity for trying it, there is little doubt that on land on which tractors or horses and implements could be used, the crop could be ploughed out, especially if a disc or other suitable cutting implement were attached in front of the plough to cut the rhizomes to a depth of about six inches. The crop could thus be separated from the earth and collected with graips. Possibly in some cases this would be an easier and cheaper method of destroying bracken on infested lands than the

laborious method of repeatedly cutting the fronds over a period of two or more years.

A large number of samples of bracken rhizomes obtained from various parts of Scotland at different times of year were analysed. The composition of a number of these is shown in Table I., and for comparison the average composition of potatoes is given.

The bracken root samples were all collected between May and August. When those obtained from Mugdock Wood were gathered, the fronds had already begun to grow though they were not yet uncurled. These samples were obtained from the locality where a few tons of the rhizomes were dug for the feeding and meal-making experiments which are described below.

Samples were also taken from two different places in rough woodland at Craibstone, the experimental farm of the North of Scotland College of Agriculture. From each of these two places, distinguished in Table II. as "A" and "B," ten samples were taken, distributed systematically throughout the whole year from the beginning of April, 1918, to March, 1919. This was done to test the variation in the composition of bracken rhizomes throughout the year. The complete results of these analyses will be discussed elsewhere, and only the average results of the ten analyses from each place are shown in Table II.

While the figures in Table II. show the average composition for the whole year of rhizomes from the two places chosen, considerable changes in composition were found throughout the year at both places. As might be expected the rhizomes

TABLE II.—Composition of Bracken Rhizomes from Craibstone. Averages, each of 10 Samples.

Series	Moisture. per cent.	Ether Extract. per cent.	Albuminoids* per cent.	Soluble Carbo- hydrates per cent.	Fibre. per cent.	Ash† per cent.	*Contain- ing total Nitrogen per cent.	*Contain- ing Protein Nitrogen per cent.	†Contain- ing Siliceous Matter per cent.
A. Original	71.10	.23	1.19	19.38	6.17	1.93	.19	.16	.93
Dry matter	—	.82	4.18	66.49	21.50	6.92	.66	.54	3.43
B. Original	70.19	.26	3.88	17.09	6.03	2.55	.62	.55	1.51
Dry matter	—	.87	13.29	56.51	20.68	8.65	2.12	1.86	5.08

became poorer both in albuminoids and in soluble carbohydrates after the growth of the fronds became active in spring. But this fall in quality lasted for two or three months only, after which the rhizomes recovered again, especially in soluble carbohydrates. Further, it is important to notice that at no time were the rhizomes exhausted, or anything like exhausted, of their food stores. Thus in the case of the "A" samples, the albuminoids at the beginning of April, before the fronds had appeared above ground, were 2.09 per cent; this fell by the beginning of June to 1.01 per cent and by the middle of July to 0.44 per cent, but by the middle of August it had risen to 1.69 per cent, and in the case of the "B" samples the corresponding figures were: beginning of April 5.36 per cent, early June 4.01 per cent, middle of July, 2.01 per cent, middle of August 3.44 per cent. This indicates that the stores of nitrogenous material in the rhizomes are drawn upon for frond formation until July, when the fronds are fully grown, and that after that storage of nitrogenous material in the rhizomes again begins.

Something similar was found in the case of the soluble carbohydrates, except that they were never reduced to nearly so great an extent as the albuminoids, and they began to increase again more quickly. Thus in the case of both the A and B samples they reached their minimum in June, and the percentage was in both cases greater in August than at the beginning of April.

These facts illustrate the necessity of cutting bracken fronds early and repeatedly if the rhizomes are to be exhausted and the plants destroyed. If cutting is delayed till the fronds are fully developed, storage of food materials has already begun again. The longer cutting is delayed after the fronds are fully developed, the more food the plant is able to store in the rhizome. On the other hand, if cutting or breaking down of the fronds is carried out before they are fully developed, the rhizome is very incompletely exhausted of its food stores, and will not have much difficulty in sending up another vigorous crop of fronds. So far as these analyses go, they indicate that the best time to cut bracken is about the middle of July, as at that time the store of nitrogenous material in the rhizomes is at its lowest, and therefore the next crop of fronds sent up is bound to be much weakened for lack of nitrogenous matter.

The analyses indicate, on the other hand, that the worst time to obtain bracken rhizomes for use as food is in July, for at that time they are lowest in the valuable food constituents, albuminoids and soluble carbohydrates, and highest in the almost valueless fibre. After July they improve in composition, and are at their best in winter and in spring, when growth is just beginning. After April they deteriorate, but samples raised in April

were as good as those obtained at any time of year.

It was found that the percentage of albuminoids varied greatly in different samples of bracken rhizomes. This is very markedly shown by the A and B samples from Craibstone (Table II.). The average of the ten B samples shows more than three times the albuminoids in the average of the ten A samples. Not only so, but every individual B sample contained a far higher percentage of albuminoids than the corresponding A sample. In some cases it was seven times as great.

Some analyses were also made of the fronds from A and B, and it was found that this peculiarity extended to them also. Fronds grown at B were much more nitrogenous than those grown at A, though the relative difference was not quite so great as in the case of the rhizomes.

(To be continued.)

NOTES.

CARNAUBA WAX.—Before the war carnauba wax was an important export from Brazil. Exports: 1916—4167 metric tons; average prices, \$4.80; 1917—3669 metric tons; average prices \$5.75. The chief exporting ports are Fortaleza and Ilha-Cagneiro, and the principal buyers the United States, Great Britain, and France.—*Matières Grasses*, Nov. 15.

LEMON SEED OIL.—The "pastazzo" or residue from washing citrate of calcium &c., in the manufacture of citric acid contains a large quantity of pips. P. Bertolo considers that this waste product, of no commercial value, could be profitably utilised for oil extracted by pressure or with solvents. By the last method the yield is 30 to 35 per cent, according to the degree of maturity. The oil from the press is light yellow and rather fluid with the odour of lemon and tart in flavour. That extracted with solvents is somewhat turbid and gives a considerable volume of pasty sediment consisting chiefly of solid saponifiable matter. The oil is semi-siccative and resembles cottonseed oil, containing a very high percentage of liquid glycerides and less than 28 per cent solid.—*Giornale Ch. Applicata*, 1920.

THE KATOKA TREE.—The commercial interest evinced this year in the edible seeds of the Katoka tree, imported from the West of Madagascar, led M. Jumelle to study the botanical origin of these seeds. The Katoka is an Artocarp which may be regarded as new and belongs to the genus *Treculia*. It is consequently akin to the Jack tree

and bread fruit tree. The Katoka is a tree which may attain a height of 30 metres. Its trunk always deeply furrowed, has a smooth grey tinted bark. It gives a large quantity of edible seeds, but with a small percentage of oil.—*Comptes Rendus*, December 8, 1920.

THE NOLI PALM.—The oil palm of South America is the *Elæis Melanococca* Gaertn. It is analogous with the *Elæis Guineensis* of West Africa, but is smaller. The flesh of the fruit represents 16 per cent; the nut 84 per cent, 62 per cent of which is shell. The flesh contains 8.1 per cent water, and 29 per cent of oil, which is equivalent to 31.5 per cent of oil in the dessicated fruit. The oil is a liquid of an orange yellow colour, with a high percentage of free skarin. It is more fluid and lighter in colour than the West African palm oil. The constants are as follows:—

	Noli Palm Oil.	W. Africa Palm Oil.
Density	0.8636	0.8586
Point of solidification	33° 6	36°—46°
Acid index	19.7	—
Saponification index	199	196—205
Iodine index	83.5	53—57
Not saponifiable	0.7 per cent	—
Soluble volatile fatty acids	0.7	0.86—1.87
Insoluble volatile fatty acids	0.5	—
The kernels contain 7.2 per cent water and 45.4 per cent oil, viz., 48.7 per cent in the dessicated seeds; it is a solid pale cream fat.		

	Noli Palm Oil.	W. Africa Palm Oil.
Density	0.8651	0.8731
Solidification	26° 9	20°—25° 5
Acid index	0.6	—
Saponification index	234	242—255
Iodine index	27.7	10.3—17.5
Not saponifiable	0.8	—
Soluble volatile fatty acids	1.4	5—6.8
Insoluble volatile fatty acids	3	10—12

—*Matières Grasses*, Nov. 15.

SELECTING OIL CAKES.—A paper by M. Ringelmann, read at the French Academy of Agriculture, deals with the selection of oil cakes. The alimentary value of a cake, he observes, is chiefly represented by its proteinous richness, but as it is to the interest of farmers to buy the food-stuff in form of cakes, we must also consider the cost of crushing, which may vary in the ratio of 1 to 5, according to the hardness of the cakes. According to his experiments, M. Ringelmann considers that the following classification may be made: *Soft Cakes*—Home-grown colza; Egyptian cotton (first crop); home-grown linseed; sesamum; red copra; coconut. *Hard Cakes*—Shelled peanuts; Egyptian cotton (second crop). *Very Hard Cakes*—Niger and white poppy. This classification, relating to the cakes tested, may certainly vary with oil mills. Briefly, the richness in protein is not a sufficient guide in selection of a cake. Cost of crushing must be estimated, i.e., the mechanical work expended on the operation. An idea can be obtained from comparative tests of cakes, ascertaining with the same machine and regulation the number of revolutions required to crush a certain weight of cakes, with examination of the volume and weight of the screened pieces, because, as far as possible, production of meal or grits must be avoided.—*Vie Agricole*, Oct. 23, 1920.

PORTLAND CEMENT AND CALCIO CYANAMIDE.—The production of ammonia and then consequently of sulphate of ammonia from cyanamide according to the equation $\text{CaCN}_2 + 3\text{H}_2 = \text{CaCO}_3 + 2\text{NH}_3$, which already before the war was greatly developed, gives a troublesome residue in form of a blackish slime which when dry turns to a noxious grey powder. According to Julius Baumann (*Chemiker Zeitung*, July 29) the Velvorde Works, near Brussels, was obliged to cease work because this by-product could not be utilised, and he considers it absolutely necessary to find some means for its utilisation in order to give a greater development to manufacture of ammonia from calcio cyanamide. Baumann considers that the best method is to employ this black slime for manufacture of Portland cement. Experiments were made in which 4.71 parts of dry slime were mixed with 1 of crushed burnt clay in a kiln, at a white heat, until quite soft. Had it been possible to employ a rotary kiln the slime could have been treated without drying. Thus, the possibility of utilising this waste product was fully demonstrated, and will benefit the industry for manufacture of ammonia from calcio cyanamide.—*Giornale di Chimica Industriale*, Nov., 1920.

THE FUEL QUESTION IN NORWAY.—According to figures issued by the Central Committee of Norwegian Scientific and Industrial Research, about 3 million tons of coal, coke, and cinder, are imported annually into Norway, this representing 20 per cent of Norway's total imports. During the year 1918-1919, 50,000 tons of coal were mined at Spitzbergen; hopes are being entertained of increasing this amount, but the town's geographical position introduces serious transport difficulties. The Norwegian waterfalls are capable of producing 15 million kilowatts, of which only 1,200,000 kilowatts are being at present utilised; half of which is used in industry, the other half is used for the running of motors and lighting. If all motors and lighting in Norway were electrified, another 1 million kilowatts would be needed.

The 3 million tons of imported fuels are equivalent to 2 million kilowatts, or 2.7 million h.p. It is, however, impossible to wholly substitute the use of fuel, for it is indispensable to steamers, in the manufacture of carbide, and for partial house-heating during the coldest part of the season. Assuming this quantity of fuel to be 800,000 tons the remaining 2.2 million tons, equivalent to 2 million h.p. should be obtained by the utilisation of water power. Other sources of fuel are the waste wood of the forests, equivalent to 1.2 million tons of coal. Norway has 12,000 square kilometres of peat land, of which about one-sixth (2000 square kilometres) is adaptable as fuel. Calculated to a depth of 2 metres, the said area will give 600 million tons of peat, equivalent to 300 million tons of coal. The Committee recommends a thorough economy with all fuel. It is suggested that a thoroughly rational firing would save 30 per cent of all the fuel now used in Norway. If we only calculate on a 10 per cent saving, this means 3 million tons of coal, a quantity not at all to be neglected. Much fuel could be saved in house-heating by more economically constructed stoves and better isolation of walls and windows. The Committee further recommends the appointment of a permanent Fuel Committee, in order to survey the economical firing in industry and households.

THE DUTCH COLOUR INDUSTRY.—The following details are taken from a report published by the Dutch Ministry of Commerce on the colour industry during the first six months of the year. "A good flow of business has been produced in lakes, varnishes, and colours, and there is a satisfactory demand from other countries. The situation is favourably influenced by the activity displayed in the building industries, especially in the devastated districts of the North of France. Dutch imports of colours and lakes were as follows. White Lead—573 metric tons, in which 276 were from Germany and 85 from America. Zinc White—1969 metric tons; 1636 being German. Red Lead—525 metric tons. Ochre—565 metric tons; 199 French, and 192 German. Other Colours—1247 metric tons. Coal Tar Colours—581 metric tons, 456 being German. Crushed Colours—278 metric tons. Lakes—52 metric tons; 35 German. Siccatives and Varnishes—102 metric tons; 6 English, and 26 United States. *Exports:* White Lead—19 metric tons. Zinc White—1062 metric tons; 494 for Belgium. Lithopone—3566 metric tons; 2793 for Belgium; 365 for France. Crushed Colours—683 metric tons. Red Lead—105 metric tons. Other Colours—1183 metric tons. Coal Tar Colours—44 metric tons. Siccatives and Varnishes—110 metric tons; 26 for Sweden, 16 Norway, 11 Denmark, 30 Dutch Indies.—*Rev. Produits Chimiques*, October 15, 1920.

MEETINGS FOR THE WEEK.

Saturday, January 1, 1921.

Royal Institution, 3. (Christmas Lectures). "The Open Sea," by Prof. J. Arthur Thomson

Tuesday, January 4.

Royal Institution, 3. "The Great Deepes," by Prof. J. Arthur Thomson.

Rhugon Society, 8.15.

Wednesday, January 5.

Royal Society of Arts, 3.

Thursday, January 6.

Royal Institution, 3. "The Freshwaters," by Prof. J. Arthur Thomson.

Society of Chemical Industry, 7.30. (At Bristol).

Friday, January 7.

Society of Chemical Industry, 7. (At Manchester).

Saturday, January 8.

Royal Institution, 3. "The Conquest of the Land," by Prof. J. Arthur Thomson.

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